SOIL CO_2 MEASUREMENTS AND THEIR APPLICATION IN KARST STUDIES

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by

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ABSTRACT

Soil CO_2 concentrations and soil temperature data were collected at the main field site, Rock Chapel Sanctuary, over a period of six months (July-December, 1981). Measurements were made under three vegetation types and at depths of 10, 25, and 50 cm beneath each vegetation type. Analysis of variance testing of the data set shows that at Rock Chapel soil temperature is not a significant source of variation in CO_2 concentrations. Furthermore depth beneath the soil, but not vegetation type, was found to be a significant source of variance in CO_2.

As a secondary part of the project the Dräger and vacutainer methods of soil air sampling were tested and compared. Both methods were found to be approximately equal in accuracy. The vacutainer method suffers from storage and internal pressure problems however it is a useful method when collecting large numbers of samples from permanent sites. The Dräger method is invaluable in remote locations and works best with small sample volumes.

The collection of soil CO_2 data should be done according to a well constructed sampling design otherwise much information regarding the effects of depth, vegetation type and other factors on CO_2 concentrations will be lost.

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CHAPTER 1

INTRODUCTION

1.1 Preamble

Gaseous carbon dioxide (CO_2) is ubiquitous within the atmosphere of the earth. On a global scale CO_2 is present in the atmosphere in quantities of about 0.033% vol. (330 ppm) near sea level. Annually this concentration remains relatively constant at any particular location but variations on the order of 5 to 15 ppm exist altitudinally. In general CO_2 concentrations decrease with increases in altitude and latitude. Higher altitudes at any latitude have less annual variation than lower altitudes, and higher latitudes have greater annual variation than lower latitudes (Woodwell, 1978).

The natural sources of CO_2 are many. Miotke (1974) offers a comprehensive review of these. Two of the major sources are production by a) respiration in living plants and animals, and b) decomposition of organic material. Both of these processes occur within the soil. Being one of the largest stores of carbon in the form of CO_2 on the earth, the soil controls, to some extent, global variations of CO_2 in the atmosphere. The soil is also a relatively consistent producer of CO_2 compared to other sources such as volcanic eruptions. Finally, because soils have formed on most of the earth's surface - that is across a variety of climatic regions - the seasonal variation in CO_2 production will influence, to some extent, annual variations of CO_2 in the atmosphere.

While the characteristics of atmospheric CO_2 are reasonably well known for several locations where long term monitoring is taking place (eg. Mauna Loa, Hawaii), the characteristics of CO_2 in the soil are not. No long term monitoring exists and only within the past several decades have intensive, short term measurements of soil CO_2 been made. In the context of karst research it is now firmly established that CO_2 produced in the soil combines with water (H_2O) to form carbonic acid (H_2CO_3). This association of compounds and its subsequent movement through a carbonate rock mass is the driving mechanism for carbonate dissolution and karstification. The modelling of groundwater chemistry in carbonate aquifers is dependent on understanding how soil CO_2 varies seasonally, and as a function of vegetation cover and depth.

1.2 Objectives of the study

There are three main objectives that this study will address. First, to provide a summary of the broad spectrum of soil CO_2 research published through the last twenty years and to draw some general conclusions from it. Second, to describe two methods of sampling and measuring CO_2 in the soil and to present data from various tests involving each of these methods. The first method uses the Dräger gas detector pump which has been used widely in karst research over the last decade or more. No research has been published, as far as the author is aware, concerning the variability and consistency of this method in the field or under laboratory conditions. The second method, which incorporates soil air sampling in evacuated glass tubes, is not unknown and appears to be as equally untested as the Dräger method. Some insight, therefore, will be gained about these methods by the tests described in later sections. Third, a model which predicts soil CO_2 as a function of soil depth is presented. The data for this model were collected over a six-month period at Rock Chapel Sanctuary near Hamilton. No such modelling has been done previously in a karst context or any other. The data set represents a relatively long term, although slightly sporadic record including soil CO_2 concentrations and temperatures measured at fixed depths and locations. Few such data sets have existed previously.

1.3 Organization

The remainder of this thesis is presented in four chapters. The second chapter contains a literature review and general conclusions drawn from the literature about the availability and variability of soil CO_2. The third chapter presents a description of the study area including bedrock and surficial geology, soils, topography, regional and local climate. Also in this chapter are descriptions of the methods and techniques used in data acquisition and also of the sampling design incorporated in the study. Chapter four describes the numerous tests applied to the Dräger and the evacuated tube methods. The results of these tests and a discussion of their consequences is given. The CO_2 model description and analysis are also presented in the fourth chapter. General conclusions regarding the objectives of the study as a whole, and areas to which future research could be directed, make up the fifth chapter.

CHAPTER 2

REVIEW OF THE LITERATURE

2.1 An historical perspective 1929-1959

Karst researchers have long recognized that aqueous CO_2 plays a role in the creation of solutional landforms in carbonate rocks. Pioneers in the study of karst such as Stockdale (1926), Swinnerton (1932), and Rhoades and Sinacori (1941), stated that CO_2 must be present in groundwaters for carbonate dissolution to occur. Others, notably Ward (1930) and Gardener (1935), suggested that limestone is quite soluable, a property that is spatially variable and dependent upon the quantity and concentration of groundwaters. Davis (1930, 613) acknowledges that CO_2 is necessary for limestone dissolution however it "... may be less important in the excavation of caverns that has generally been believed ...". Davis' statement was, unfortunately, based on tenuous observations. Although an understanding of the basic solution chemistry was known during the formative years of North American karst research (see Frear and Johnston, 1929), knowledge of the nature of soil CO_2, in particular its availability and variability, was not known.

In one of the first quantitative karst studies a French scientist, Schoeller (1950), described the variation of CO_2 in groundwaters. Using data collected in the Alps and Pyrenees, Schoeller found that CO_2 in groundwaters decreased with increasing altitude. He suggested that increasing latitude could be substituted for increasing altitude and therefore polar regions would have less CO_2 in their waters than temperate regions. In contrast to this Corbel (1957, in Atkinson and Smith, 1976) suggested that arctic waters would dissolve more limestone than tropical waters because CO_2 has a greater solubility in cold water. Schoeller, unlike Corbel, recognized that the major source of CO_2 in groundwaters, the soil, became less productive at colder temperatures. In a laboratory study of the solubility of calcium carbonate Weyl (1959) found that solution or precipitation could only take place as a result of changes in temperature, pressure, or the chemical composition of the water. This work by Weyl was significant in that it represented the first of a series of papers, by several authors, dealing with the kinetics of the solution process. It also prefaced, by about two years, a dramatic increase in research on the measurement of CO_2 in the soil.

2.2 The Measurement of Soil CO_2 1961-Present

2.2.1 Introduction

It has been well documented in the literature that soil CO_2 concentrations are higher than atmospheric concentrations. Daubenmire (1974) cites values as high as 13% in natural soils. Concentrations greater than 3% to 4% are rare, however, particularly in temperate regions. As the scale of investigation is reduced, for example to an area the size of a football field, the temporal and spatial variability of CO_2 increases. The production of CO_2 by respiration and decomposition will become dependant upon short term, day to day climatic events, and also on more stable physical characteristics of the soil, such as depth and grain size.

Much has been written about the variability of CO_2 as a function of any number of physical and climatic parameters. The majority of papers cited in this chapter come from the disciplines of soil science, ecology, and forestry. A much more general overview of soil CO_2 literature is given by Gunn and Trudgill (1982). These authors recognize three major divisions of soil CO_2 data; those used in studies of a) pedology/soil ecology, b) karst geomorphology, and c) groundwater hydrology/geochronology. It will suffice to say that much of the karst researchers understanding of soil CO_2 comes from outside the present scope of karst research.

2.2.2 Some Methods of Soil CO_2 Measurement

Because soil CO_2 data can be drawn from several disciplines, the purposes for which it is collected vary. As a consequence of this, methods of measuring the amount of CO_2 in the soil are numerous. One important distinction among data sets from other sources should be made. Many ecological studies measure the amount of CO_2 given off by the soil at the surface. This allows calculations of soil productivity and biomass to be made. Other studies measure the concentration of CO_2 at some depth beneath the surface of the soil. The latter methodology is the one employed in this study.

Campbell and Frascarelli (1981) have distinguished four frequent measures of CO_2. These are 1) CO_2 evolved from the soil surface in situ, 2) CO_2 evolved from disturbed samples in the laboratory, 3) CO_2 concentrations measured at depth in the soil, and 4) CO_2 measured in groundwaters. The majority of CO_2 measurements in the soil science/ecology/forestry literature are made using Campbell and Frascarelli's first measure; CO_2 evolved from the soil surface. Such measurements require placing a container, usually a cylinder but sometimes an inverted box, into the soil. The depth of insertion is usually shallow, 10 cm or less, because researchers who use this method are often concerned only with the LFH horizon of the soil. After insertion CO_2 evolved from the soil may be measured several ways. The simplest way is to absorb the CO_2 in potassium hydroxide (KOH) when a measurement is required. Barium choloride ($BaCl_2$) is then added to the KOH and the solution is titrated to an end point with hydrochloric acid (HCl). Anderson (1973) advocates this method which is used also by Brown and MacFayden (1969). Variations on the KOH/$BaCl_2$/HCl combination exist. Reinke et al (1981) substitute sodium hydroxide (NaOH) for KOH as do Campbell and Frascarelli (1981), Lieth and Ouellette (1962), and Wildung et al (1975). As an alternative to chemicals some researchers utilize infrared gas analysers (Kanemasu et al, 1974; Garrett and Cox, 1973; Edwards, 1975; Redman, 1978; Sheihk, 1969; Billings et al, 1977; Kelley et al, 1977; Reiners, 1968) or gas chromatography (Yamaguichi et al, 1967; DeJong et al, 1974). DeJong and Schappert (1972) used permanent diffusion wells which could be sampled with disposable syringes and the contents analysed with gas chromatography. Campbell (1974) and Reardon et al (1980) used similar arrangements.

Recent karst research which has incorporated soil CO_2 measurements has relied, fairly exclusively, upon the Dräger device described by Miotke (1974). The Dräger cannot be used to measure soil respiration or CO_2 evolution rates from the surface and as such has not been used in the soil science/ecology fields. Brook (1976), Fish (1978), Miller (1981), and Mills (1981) have used the Dräger in a range of environments, from sub-arctic to tropical. James et al (1975) describe a number of methods for measuring CO_2 in caves. It would be a simple matter to collect soil air samples, via diffusion wells as in DeJong and Schappert (1972) in order to use these methods. Miotke (1974) describes several methods of measuring soil air CO_2, including the Drager method, which are paralleled somewhat by those described in James et al (1975).

As an aside it has been noted that no uniformity exists in reporting the rates of CO_2 evolution. Comparisons of data collected by different authors are made difficult by this. Many evolution data are given in units of $g/m^2 \cdot day$ and $g/m^2 \cdot hour$. Rates in $mg/m^2 \cdot hour$ and $mg/cm^2 \cdot week$ and even $mg/dm^2 \cdot hour$ exist, as do concentrations of CO_2 in atmospheres, volume %, ppm, and $- \log PCO_2$. The most unreasonable units have been used by DeJong et al (1974). These authors report CO_2 evolution in 10^{-8} $g/cm^2 \cdot sec$.

2.2.3 The Temporal Variability of Soil CO_2

Concentrations of CO_2 in the soil are affected by annual climatic changes. Where seasonal climatic differences are great the variation of CO_2 will be great. Where seasonal differences are small, as in the tropics, the annual variation of CO_2 will be small.

Diurnal changes in CO_2 concentrations are probably controlled by a broader range of climatic and physical parameters than annual changes. For example, whereas the effect of strong winds over a period of several days will not alter the annual cycle or measurement of CO_2 production, the increased ventilation of the soil surface by such winds may reduce CO_2 concentrations measurably on a daily time scale. Extreme conditions of precipitation and temperature undoubtedly effect daily CO_2 variations although such variations are likely obliterated by seasonal changes.

Any modern study of soil CO_2 contains a temporal element within it as well as some other complicating factor such as vegetation cover. In order to present a quantitative view of annual and diurnal CO_2 variations a limited number of studies will be cited. These may be considered representative of the literature as a whole. To achieve a reasonable understanding of temporal CO_2 variations excessive repetition of the literature is unnecessary. The results given here should not be compared to one another either. Differences in technique and location exist between these studies, furthermore all are not measuring the same portion of the soil.

In the United Kingdom Anderson (1973) measured an annual range of CO_2 evolution of approximately 450 $mg/m^2 \cdot hour$ (100-550 $mg/m^2 \cdot hour$) under a beech forest. The annual trend was characterized by a distinct drop in CO_2 evolution towards the end of September. Reinke et al (1981) working in a South Carolina pine forest found annual variation on the order of 300 $mg/m^2 \cdot hour$ (75-375 $mg/m^2 \cdot hour$ - recalculated from $g/m^2 \cdot day$). Reinke et al (1981) have a shorter sampling interval and their results show greater seasonal variation than do Anderson's. Gupta and Singh

(1981) measured annual respiration within a range of 325 $mg/m^2 \cdot$ hour (50-375 $mg/m^2 \cdot$ hour) on a tropical grassland in India. On a North American temperate grassland (Missouri) a range of 450 $mg/m^2 \cdot$ hour was measured (0-450 $mg/m^2 \cdot$hour) by Kucera and Kirkham (1971).

Unfortunately the results of CO_2 respiration/evolution studies are not in units transformable to karst research. The data quoted above do provide some idea of the range of values that exist. Gunn and Trudgill (1982) found a range of about 0.5% to 2.0% V CO_2 in New Zealand at depth in the soil (20-40 cm). Richter and Jacobs (1972), as reported by Miotke (1974), found a similar annual range in a European soil, 0.25% to 2.0% V. In general the range of annual values found by ecologists at the surface of the soil and by other researchers at depth in the soil are all of the same order of magnitude. Maximum values are about four to ten times the minimum values. Maximum values are reached in late summer or early fall. Minimum values usually occur during winter. Some researchers have recognized spring and fall CO_2 thresholds, a characteristic more commonly found in temperate regions. These thresholds correspond roughly to the onset of the growing season and the first fall frost (Cowell and Ford, 1975; 1980).

Diurnal variations, as mentioned previously, are subject to a broader range of relatively short term influences. Because of this it is not possible to compare results from diurnal studies with results from annual studies. Doing so would result in ambiguous and meaningless conclusions. As plants respire only in the presence of sunlight it is expected that maximum CO_2 concentrations or rates of evolution will occur late in the day and minimum concentrations will occur sometime during the night. Edwards (1974) measured a range of CO_2 evolution rates from about 250 to 650 mg/m^2· hour in a deciduous forest in Tennessee. Maximum and minimum values occured at 9:10 pm and 5:30 am respectively. Jakucs (1971) as reported by Miotke (1974) found a daily range of about 1.75% V (0.25-2.0) in a sinkhole in Croatia.

Temporal variations of soil CO_2 are, obviously, dependent on enough factors that direct comparisons of data are difficult to make. To alleviate this problem requires comparison of conclusions formed by the many researchers who have collected CO_2 data. To this end the remainder of this chapter is devoted to reviewing relationships and conclusions found in the literature. Specifically relationships between soil CO_2 and temperature will be highlighted.

2.2.4 The Spatial Variability of CO_2 in the Soil Profile

Carbon dioxide is not produced uniformly throughout a soil profile. The depth of root penetration by vegetation creates a zone of CO_2 production as a result of root respiration. The decomposition of organic matter also releases CO_2 but organic matter is usually found in the surface horizon (LFH) or somewhere within the depth of root penetration. By what process or processes, then, can CO_2 move from zones where it is produced, those near the soil surface, to zones where it is not produced, those usually deep in the mineral soil? Current research suggests two major processes; mass flow and diffusion (Currie, 1970, Troeh et al, 1982). In mass flow CO_2, or any gas, "... moves in response to a gradient in total pressure ..." (Currie, 1970, 152; Troeh et al, 1982, 239). In diffusion "... molecules diffuse at random by virtue of their own thermal energy, and the net flow is dependent on the existence of a partial pressure or concentration ... gradient." (Currie, 1970, 152). Troeh et al (1982) consider diffusion to be the main process of gas exchange between the soil and the free atmosphere.

Little research has been done dealing specifically with measuring CO_2 variations through a soil profile. Several studies on artificial soils have been attempted. Enoch and Dasberg (1971) concocted five soils varying in grain size, natural organic matter, and $CaCO_3$ content. Their purpose was to investigate soil air composition in soils where extreme values could be expected. By measuring CO_2 concentrations (volume %) at four depths, 5 cm, 15 cm, 32.5 cm and 47.5 cm, Enoch and Dasberg were able to establish gradients with depth over a period of more than two months. In general they found that as the clay content of their artificial soils increased, the depth of the maximum CO_2 concentration decreased. These results may be tenous since the maximum concentrations Enoch and Dasberg measured exceeded 40% CO_2 in four of five soils. In one of these soils a concentration of 97.7% CO_2 was measured. It is highly improbable that such extreme values could exist in natural soils. Drake (1980) discusses the theory behind such a restriction. In any case Enoch and Dasberg find no consistent trend with depth in any of their soils.

Yamaguichi et al (1967), also using artificial soils, measured CO_2, O_2 and N_2 at depths of 5 cm, 35 cm and 65 cm, and at different temperatures. The maximum concentration encountered was about 18%

CO_2. In general CO_2 concentrations were less than 5%. A strong relationship between depth and CO_2 concentration exists in Yamaguichi et al's soils at all temperatures (10°, 15°, 20°, 25°, $30^\circ C$). Except during the first 5 to 10 days of the six month experiment, CO_2 concentrations were greatest at 65 cm and smallest at 5 cm. The 35 cm depth had intermediate concentrations.

In a study of natural soils, Boynton and Compton (1944) measured CO_2 concentrations at one, three and five foot depths in three orchard soils of different grain size composition. Like the study by Yamaguichi et al (1967), Boynton and Compton measured an increase in concentration with depth. In general their values did not exceed 5% CO_2 at the one and three foot depths. At five feet concentrations as great as 9% are shown.

2.2.5 The Relationship of Soil CO_2 with Soil Temperature and Other Parameters

2.2.5.1 Introduction

The spatial and temporal variations of soil CO_2 are rarely studied on their own. Usually these variations are monitored in conjuction with soil temperature and/or soil moisture. Comparisons of CO_2 variations with temperature and/or moisture invariably lead to the prediction of soil CO_2 as a function of temperature and/or moisture. Other less quantifiable factors, such as vegetation cover, slope and aspect are sometimes used to explain CO_2 variations. Comparisons between studies are made difficult because soil CO_2 is measured as a function of a wide range of variables.

2.2.5.2 The Behaviour of Soil Temperature

The behavior of annual soil temperatures at any given site is due largely to variations in solar radiation, air temperature, soil water content, and snow cover (Ouellet, 1972; Ouellet and Desjardins, 1975). Soil temperature is also effected by the vegetation cover, or lack of it, at a place. Baver et al (1972), cited in Toogood (1979), suggests four main effects that vegetation has on soil temperature. These are : 1) the albedo of the vegetation, 2) the depth of penetration of global radiation through the canopy, 3) the latent heat gain or loss through evapotranspiration, and 4) the heat loss of the soil through the insulating effect of the vegetation. Qashu and Zinke (1964) state that the main process of heat transfer in the soil is by molecular conduction, but soil water movement can alter the soil temperature considerably.

Ouellet and Desjardins (1975) found that the variability of minimum monthly soil temperatures is greatest at the surface and decreases with depth. Qashu and Zinke (1964) have found that, regardless of vegetation type, the greatest temperature variations occur at the surface of the soil. This variability also decreases with depth. Furthermore, a time delay with depth exists for temperatures measured in the soil. Toogood (1979) working near the city of Edmonton, found a lag of six to eight weeks between the minimum daily soil temperature at 100 cm and the minimum daily air temperature. Finally, Wildung et al (1975) discovered that daily fluctuations in air temperature went undetected at 10 cm depth in the soil.

2.2.5.3 The Effects of Soil Temperature and Other Factors on CO_2

Soil temperature varies with soil moisture content. It has also been shown that soil moisture, in the form of a rain event, can effect soil temperature. The relationship between soil CO_2 and temperature, or CO_2 and moisture is masked somewhat by the interdependence of temperature and moisture.

It is generally recognized that as soil temperature and moisture increase the biological activity in the soil increases and more CO_2 is produced. Wiant (1967b) suggests that every 10°C increase in soil temperature between 20°C and 40°C would result in a doubling of CO_2 production ($Q_{10} = 2.0$). This temperature-productivity function was first recognized by Chang (1958, cited in Toogood, 1979) when he applied the V'ant Hoff Law regarding chemical reaction rates, to soils. Although the productivity of CO_2 may double within a certain temperature range, the concentration of CO_2 at depth or its evolution from the surface may not necessarily double. Furthermore what level of productivity can be expected below 20°C? In temperate or colder regions soil temperatures may exceed 20°C only for short periods near the surface. Billings et al (1977) measured CO_2 evolution in the top 10 cm of soil near Barrow, Alaska. Under controlled temperature conditions, -1°C to 19°C, they found linear relationships between root growth in three species and temperature. In general Billings et al (1977) found diurnal variations in CO_2 evolution were linearly related to soil temperature but seasonal variations became curvilinear with temperature. Soil temperatures between 7°C and 22°C show values of $Q_{10} > 2.0$ (Billings et al, 1977, 135). Also at Barrow, Kelley et al

(1968) measured CO_2 at the soil surface over twelve months. Maximum monthly values were recorded in December (346 ppm) and minimum monthly values in September (322 ppm). They suggest that this apparent reversal of seasonal trends is controlled, to some degree, by snow depth and wind speed.

In a temperate forest in Minnesota Reiners (1968) was able to explain 75-90% of the CO_2 evolution variations by using soil temperature and moisture. The relationship between soil temperature and CO_2 evolution appears exponential over a range of 22°C (0-22°C). Variations in CO_2 evolution were greater at higher than at lower temperatures. Reiners suggests this is due to the soil moisture which is more variable under warmer conditions than under cold, frozen or partially frozen, conditions. He also found that temperature and moisture were, in general, highly correlated. As such the real effect of moisture on CO_2 was difficult to determine statistically.

Reinke et al (1981), working in a South Carolina pine forest, have explained CO_2 evolution variations using ambient air temperature, the rain falling within three days prior to CO_2 sampling, and the rain falling four to seven days prior to sampling. Using multiple regression the resulting equation was significant at the 99.9% confidence level ($R^2 = 0.64$). On an annual basis the ambient air temperature factor is three times more important than the first rainfall factor (days 1-3), and eight times more important than the second rainfall factor (days 4-7). In a variety of forest types, pine, oak and maple, in Tennessee Witkamp (1966) found CO_2 evolution to be significantly correlated with temperature, litter age, and moisture content, in order of decreasing importance. He also found that CO_2 variations could be more fully explained in the maple forest than in the pine forest using these three factors. Similarly variations within the pine stand were more fully explained than variations in the oak stand. No significant differences exist between the forest types with respect to CO_2 evolution. Temperature, however, can be more significantly correlated with CO_2 in the maple and pine stands ($P < 0.01$) than in the oak stand ($P < 0.05$). In a later study Witkamp (1969) documents a pre-dawn surge of CO_2 from the soil. He attributes this surge to soil temperatures exceeding air temperatures at night, with the resultant movement of CO_2 being due to thermal convection rather than the processes of mass flow and diffusion.

Using mean monthly CO_2 fluxes and mean monthly soil temperatures, Monteith et al (1964) could not distinguish a definite relationship between them. Both measures were made on bare soil suggesting that a vegetative cover is important to describing evolution-temperature relationships.

In a tropical environment Schulze (1967) determined significant differences in soil respiration from different forest types. Although he measured soil temperature no attempt was made to correlate it with respiration. Interestingly Schulze found a correlation between soil respiration rates and earthworm presence. He suggests that earthworms are an indictor of soil productivity - earthworms mean a more productive soil and a higher respiration rate. A more comprehensive study by Gupta and Singh (1981) in a tropical grassland shows significant independent relationships between soil respiration and soil water, rainfall and temperature. These latter three factors can explain 35%, 12% and 48% respectively of the variation in soil respiration. Multiple regression analyses by Gupta and Singh using temperature and soil water were able to explain 66% of the soil respiration variation. In western Malaysia Crowther (1982) measured CO_2 at 15 cm, 30 cm and 60 cm depth and soil moisture at 15 cm. He found that by using the rainfall from periods of 32 or 64 days prior to CO_2 sampling, up to 69% of the CO_2 concentration variation could be explained at 15 cm. At 30 cm and 60 cm, 64% and 20% respectively of the variation could be explained by previous days rainfall. Perhaps in locations where seasonal temperature differences are small, other characteristics of the environment are more useful for predictive purposes.

Garrett and Cox (1973) examined position on a slope as a controlling factor of CO_2 evolution. Working in an oak-hickory forest in Missouri, they used three slope positions for CO_2 measurements. Despite the fact that slightly different CO_2 concentrations are found at upper, middle, and lower slope positions the effect of position on CO_2 is statistically insignificant. On a slope of larger scale, differences in soil depth, soil development and drainage may create variations in CO_2 along a slope. As well, microclimate could play a role in controlling CO_2 evolutions on slopes.

2.3 Some General Comments

Unique among the soil science/forestry/ecology papers examined was that by Lieth and Ouellette (1962). These authors alone recognize, or at least make reference to an important loss of CO_2 from the soil.

"Well-drained soils with a steady flow of water may lose a great deal of CO_2 with the water going to the ground water level." (Lieth and Ouellette, 1962, 128). The proportion of CO_2 evolved in the soil which is lost by this process is unknown, but it is the cause of some degree of underestimation of total CO_2 evolved within a soil profile. Although CO_2 incorporated in groundwater flows does not contribute to soil respiration measured at the surface, it remains a result of the biological productivity of the soil and contributes significantly to the aggressiveness of groundwaters. Atkinson (1977) has expanded this idea in one direction. He has proposed the concept of 'ground air', a region where CO_2 concentrations are greater than those measured in the soil. The seasonal variability of soil CO_2 in temperate region soils varies much more than spring PCO_2's, and soil CO_2's are usually less than spring PCO_2's. The presence of a region or zone of elevated and relatively constant CO_2, ground air, can explain such discrepancies.

One recent karst study (Crowther, 1982) has concluded that the ground air concept of Atkinsons' is not operating at a particular location, western Malaysia. Crowther (1982) measured soil CO_2 concentrations and compared them to the calculated PCO_2's of groundwater seepage. Mean soil CO_2 concentrations were found to be about 1/3 that required to reach mean Ca^{2+} hardness' in the groundwater. Crowther (1982, 51) believes the soil air he sampled is "... unrepresentative of the air with which soil waters come into equilibrium during periods of groundwater recharge." Therefore, the ground air theory is not applicable to this case.

Although this single reference should not be considered a condemnation of the ground air theory it points out that alternative explanations to the theory exist. In general, soil CO_2 measured at the bedrock-soil interface may not be great enough to explain higher and more constant spring PCO_2's. The movement of groundwater in response to the development of a gradient towards a spring point could, however, influence the movement of the soil atmosphere. If this occurs then groundwaters moving to a spring may be exposed to a slightly increased flux of CO_2. As such the PCO_2 of the spring could be greater than the measurable soil CO_2. Alternatively calcium may be added to the soil by throughfall in forests (Madgwick and Ovington, 1959; Henderson et al, 1977). Calcium of this nature may be carried by groundwaters to springs. The Ca^{2+} hardness of the spring as a result of carbonate dissolution, either in the soil or in bedrock, would be overestimated.

Much is known of the characteristics of soil CO_2 in the surface (1 to 2 meters) of soils. Hydrogeologists too are well aware of the temporal and spatial characteristics of carbonate water chemistry. In a more complete understanding of the link between soil CO_2 and carbonate water chemistry lies a better understanding of the broad controls of the solutional process.

CHAPTER 3

DESCRIPTION OF THE STUDY AREA AND DATA AQUISITION

3.1 Study Area Characteristics

3.1.1 Location and General Description

Most field research for this study was performed at Rock Chapel Sanctuary, part of the Royal Botanical Gardens. Rock Chapel is located in the Region of Hamilton-Wentworth just north of Dundas. It includes an area of some 70 hectares above and below the Niagara Escarpment. Most of the Sanctuary is forest although some portions on top of the escarpment are grass covered, and other portions are regenerating to forest naturally, at present forming areas of rough scrub. Within the forest covered areas a variety of species are found including some that are typical of Carolinean climax forests. A list of tree species found at Rock Chapel is given in Appendix I. The forested area is, in general, composed of a mature, undisturbed stand of trees.

Data were also collected at several other locations in Hamilton-Wentworth. These additional sites are forest covered although probably by second or third growth which has included coniferous as well as deciduous species. The location of the main study area (Rock Chapel) and the additional sites are shown in Figure 3.1.

3.1.2 Bedrock Geology

The bedrock underlying all of Hamilton-Wentworth (and southern Ontario) was formed during the Paleozoic era. Within Hamilton-

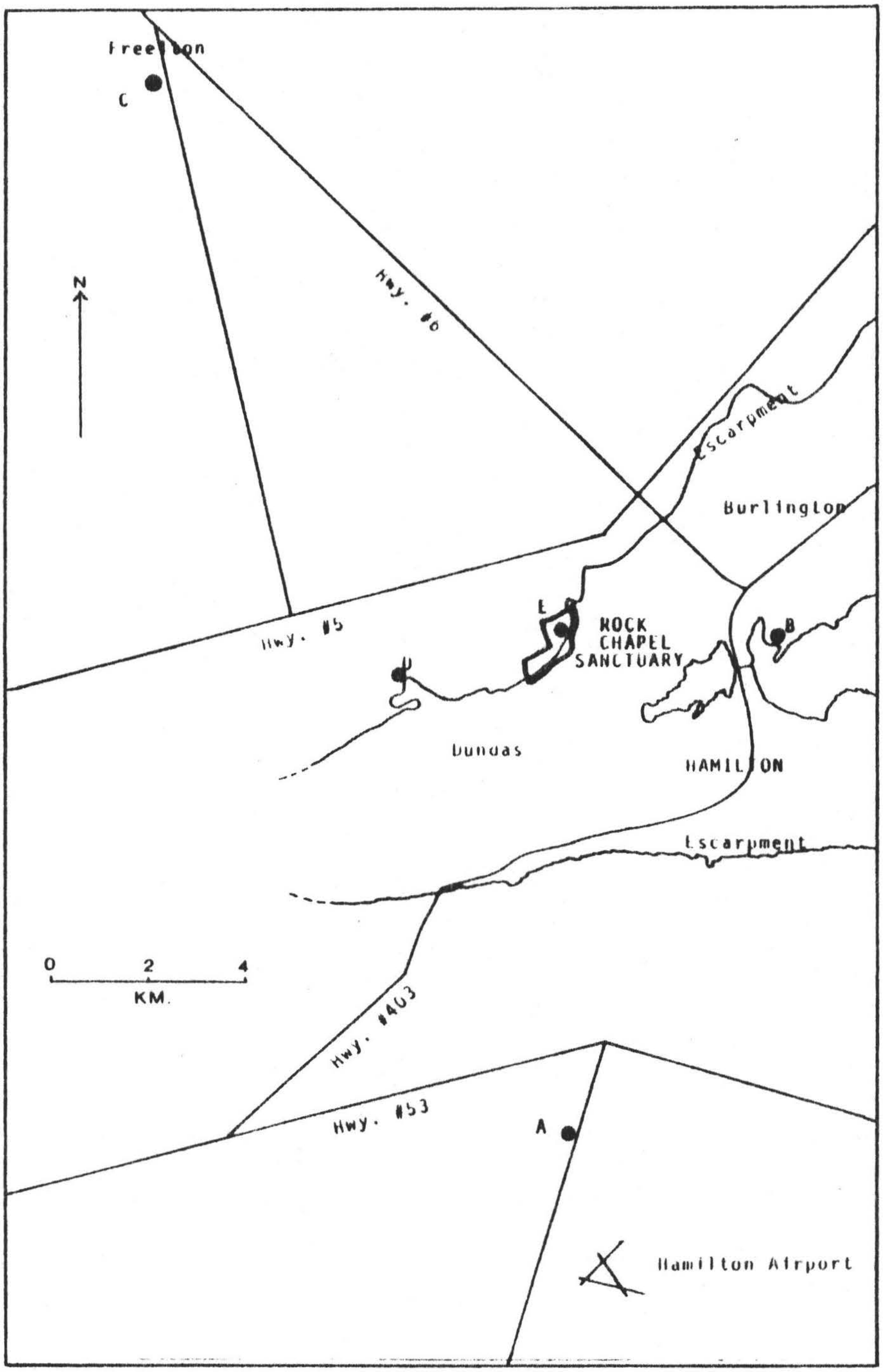

FIGURE 3.1 Location of the Study Sites

Wentworth the rocks include those from Upper Ordovician to Middle Silurian age. The formation immediately underlying unconsolidated deposits below the escarpment is the Queenston, a red shale of Upper Ordovician age. Stratigraphically overlying the Queenston Formation are, in order of decreasing age and increasing elevation, the Clinton and Cataract Groups (Lower Silurian) which are mainly dolomites and limestones with some shales and sandstones and the Lockport and Guelph Formations (Middle Silurian) which are composed predominantly of dolomites and limestones (Hewitt, 1972).

The Queenston forms the lowest unit of the escarpment, but because of mantling by till, talus, and glaciofluvial material it is not exposed. The other formations are visible along the escarpment at numerous locations including Rock Chapel. Individual members of the formations are not continuous along the escarpment (Bolton, 1957) due presumably to a variable depositional environment, although some unconformities are known to exist. A generalized geological column is shown in Figure 3.2.

Data collection sites within Rock Chapel and at three of the four additional sites (A, C and D on Figure 3.1) are located on top of the escarpment and, therefore, are on either the Guelph or Lockport carbonates. The remaining additional site is below the escarpment and is located on the Queenston shale.

All formations above the Queenston dip to the southwest at approximately 6.25 m/km (33'/mile) throughout the Hamilton region (Liberty and Bolton, 1956). The elevation of the top of the escarpment ranges from 192 meters (630') in Hamilton, to 201 meters (660')

Figure 3.2 Generalized Bedrock Geology of the Niagara Escarpment from Hamilton to Clappison Corners.

Period	Formation or Group	Member	Dominant Lithology	Thickness in Metres (Hamilton-Clappison Corners)
Middle Silurian	Guelph		Dolomite	2.1 - 3.0
	Lockport	Ermosa	"	13.1 - 17.7
		Goat Island*	"	2.7 - 11.0
		Gasport	Limestone	2.4 - 6.1
Lower Silurian	Clinton	DeCew*	Dolomite	1.8
		Rochester*	Shale	0.6 - 4.3
		Irondequoit*	Limestone	1.2 - 2.1
		Reynales*	Dolomite	2.1 - 3.0
		Thorold*	Sandstone	4.0
	Cataract	Grimsby*	Shale & Sandstone	3.7 - 8.8
		Cabot Head	Shale	10.4
		Manitoulin	Dolomite	3.4
		Whirlpool	Sandstone	3.7
Upper Ordovician	Queenston		Shale	150

* Present at Rock Chapel

After Bolton(1957)

at Rock Chapel,up to 213 meters (700') at Clappison Corners located several kilometers east of Rock Chapel.

3.1.3 Surficial Geology

A comprehensive account of the Pleistocene geology of the Hamilton region, including the study areas, is given by Karrow (1963). Straw (1968) has also published a description of the surficial landforms in this region which he states to be a more viable sequence of late Wisconsin and post-glacial events than those of Chapman and Putnam (1966) or Harris (1967).

The surficial material on top of the escarpment is the Halton till (Karrow, 1963). It was deposited in the late Wisconsin at least 12,000 years B.P. during the last advance of an ice lobe westward into the Lake Ontario basin. The depth of till increases away from the escarpment. It ranges from zero at the crest to 50 cm depth 30 to 100 meters back (north) from the crest, to well over a meter and probably several meters deep 300-400 meters from the edge of the escarpment.

Analyses published by Karrow (1963) of 34 samples of Halton till indicate it has an average grain size distribution of 25.2% sand, 35.6% silt, and 39.2% clay. Heavy minerals including hornblende, clinopyroxene, magnetite-ilmenite, white and purple garnet, red-orange garnet, and hyperstene are present in the till. Their occurrence indicates that Halton till is not derived entirely from local bedrock such as the Queenston shale and the Silurian carbonates. Despite this, surficial deposits will have been influenced to a greater or lesser extent by these local lithologies.

3.1.4 Soils and Topography

Since deglaciation surficial deposits have undergone extensive alteration in undisturbed locations. These alterations are due largely to the processes of physical and chemical weathering. The end result of these processes has been the development of a suite of identifiable soils. Presant et al (1965) have described and analysed these.

Within a kilometer or two of the escarpment the soils are largely gray-brown podzols or brown forest brunisols and are slightly to moderately stoney. pH ranges from 6 to 8 but is usually more acidic than basic. The topography along the top of the escarpment is mainly complex, that is having multiple slopes, although at Rock Chapel simple, single slopes dominate. Slope angles are generally shallow, less than 5%, but may be 15% and 30% in some cases. Table 3.1 shows these characteristics for Rock Chapel and each of the additional study sites.

3.1.5 Regional and Local Climate

The climate of southern Ontario is influenced to a large extent by the presence of the Great Lakes and by prevailing winds and variations in topography (Brown et al, 1968). Despite the presence of the Great Lakes, which act to moderate temperatures, the climate of the region is considered to be continental (Hare and Thomas, 1979). Precipitation is distributed fairly uniformly throughout the year (Chapman and Brown, 1966), and averages approximately 5 to 10 cm/month (Brown et al, 1968). About 15% to 30% of the annual precipitation falls as snow. Temperatures vary considerably throughout the year. Mean annual air temperature ranges from about 5°C to 9°C in southern Ontario.

Table 3.1 Bedrock, Soil and Topographic Characteristics of the Study Sites

Site	Elevation (±7 m)	Bedrock[1]	Soil Type[2]	Slope[2]
A - Hamilton Airport	241 m	Guelph Dolomite	Toledo Silty Clay Loam (To)	Complex 0.5-2.0% (Multiple Slopes)
B - Carrolls Point	76 m	Queenston Shale	Grimsby Sandy Loam (Gi)	Complex 16-30%
C - Freelton	267 m	Lockport Dolomite	Donnybrook Gravelly Loam (Dk)	Complex 16-30%
D - Websters Falls	229 m	Lockport?/Guelph?	Ancaster Silt Loam (An)	Complex 16-30%
E - Rock Chapel	206 m	Lockport Dolomite	Farmington Loam (Fl)	Simple (Single Slope) 2-5%
	209 m		Chinguacousy Loam (Cl)	Complex 2-5%
	213 m		Oneida Loam (Ol)	Complex 2-5%

[1] after Hewitt (1972)

[2] after Presant et al (1965)

January mean daily temperatures range from about -12°C to -3°C and July mean daily temperatures range from about 18°C to 22°C (Brown et al, 1968).

In order to describe the main study area, Rock Chapel, in specific climatic terms, observations from Hamilton Airport (see Figure 3.1) are used. Both locations have similar elevation, topography, aspect, and exposure to prevailing winds. Monthly maximum, minimum and mean temperatures for the period 1931-1960 and for 1981, the year during which the study took place, are shown in Figure 3.3. Figure 3.4 displays monthly precipitation for similar periods.

Results of comparisons of normal values with those for the period during which field measurements were made (June to December, 1981) may be summarized as follows:

1. The field season (June to December) was slightly cooler than normal (11.7°C vs. 12.1°C)

    a) June, July and August means were within 0.1°C of normal
    b) September and October were cooler than normal
    c) November and December were warmer than normal

2. the field season was much wetter than normal (777.2 mm. vs. 473.2 mm.)

    a) approximately twice as much rain fell in July, August and September than normal (505.4 mm. vs. 216.4 mm.)
    b) the other months were relatively close to normal.

Observations of daily temperature and precipitation at Hamilton Airport during the field season are shown in Appendix II.

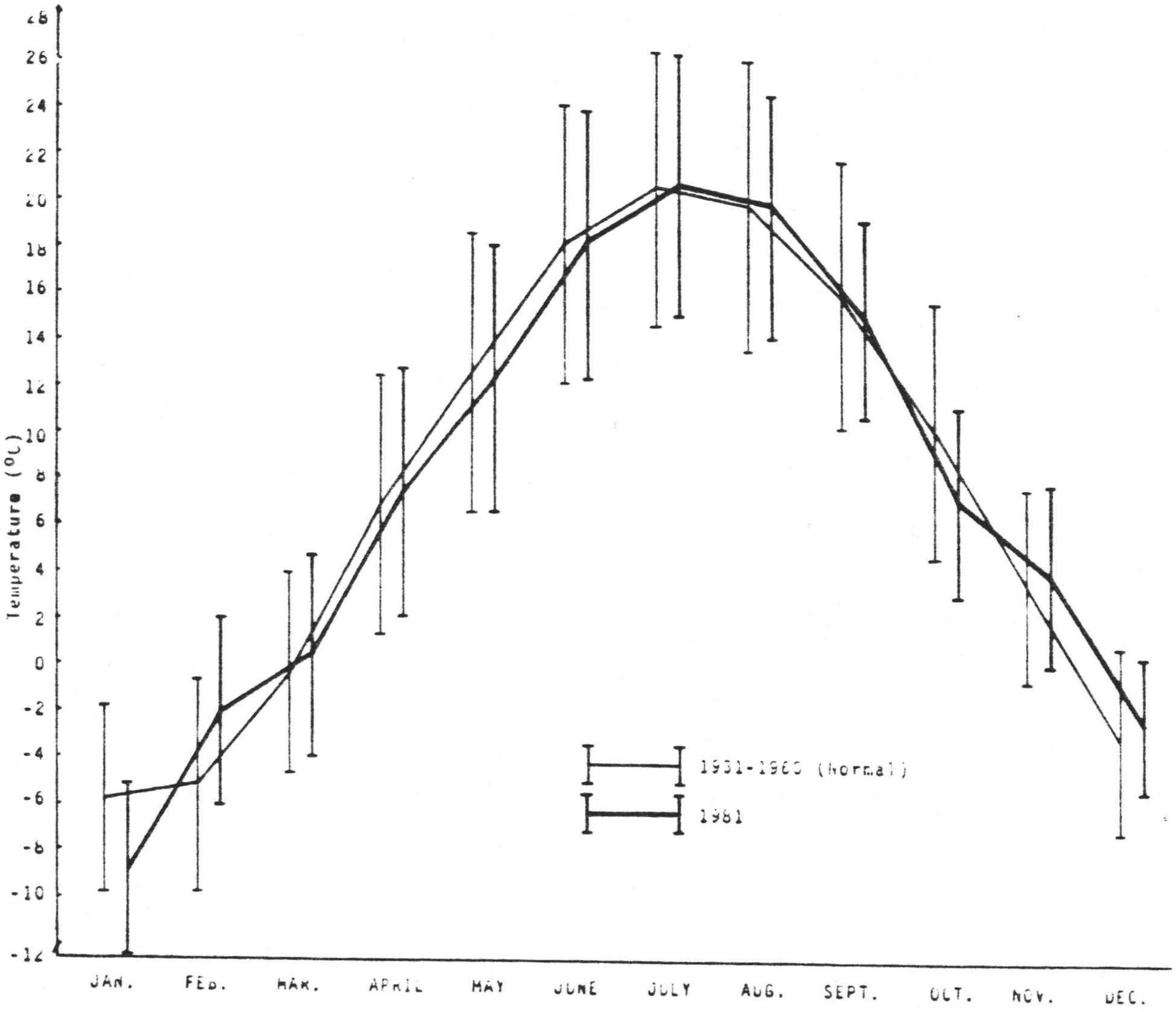

FIGURE 3.3 Maximum, Minimum, and Mean Monthly Temperatures - Hamilton Airport

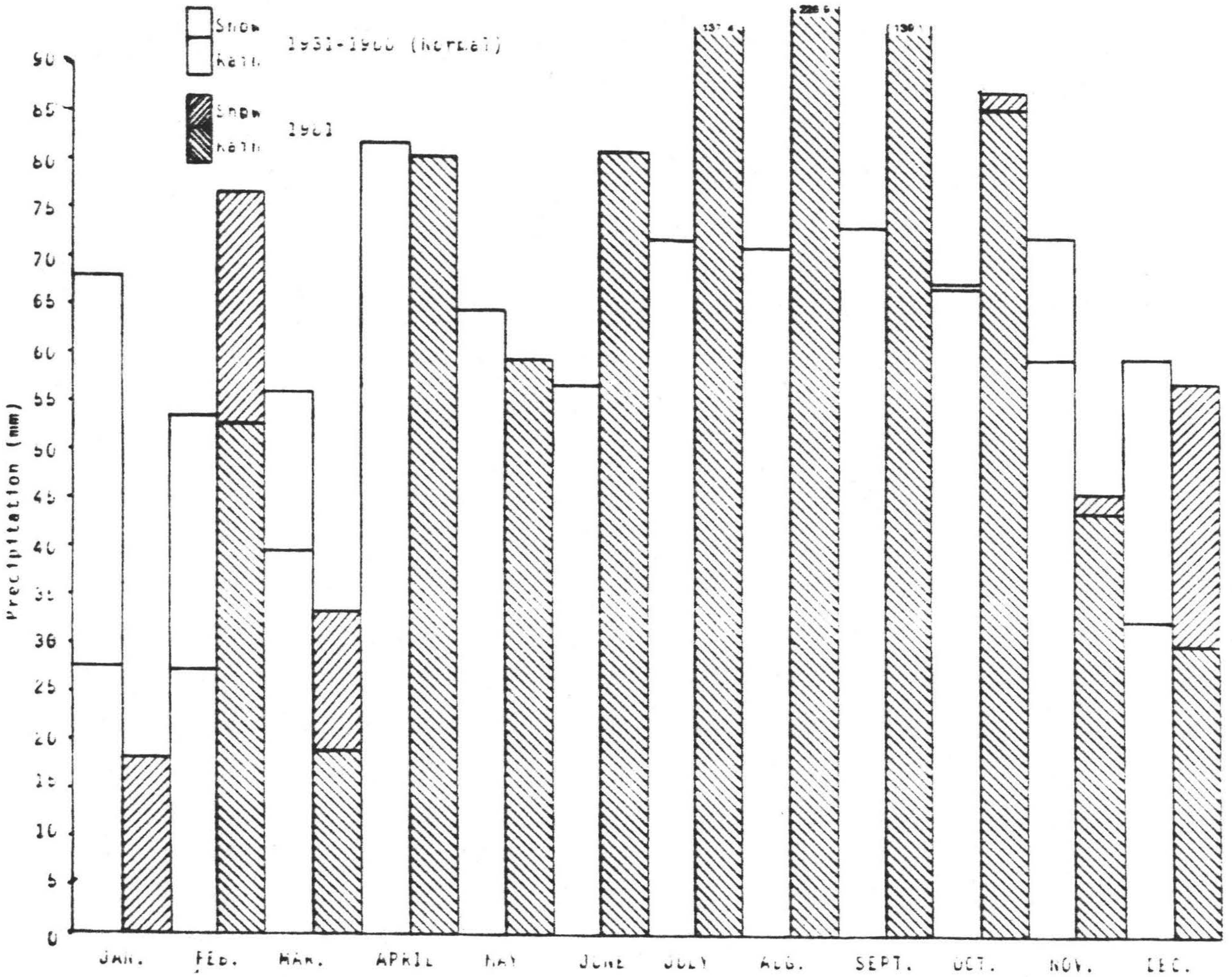

FIGURE 3.4 Monthly Precipitation - Hamilton Airport

3.2 Data Aquisition

In this section technical aspects of the instruments, methods and techniques used at various stages of the research are described. These descriptions are divided into two sections; those concerning the measurement of soil temperature and those concerning the measurement of CO_2. The sampling design at Rock Chapel and the additional sites are also described.

3.2.1 Soil Temperature

3.2.1.1 Field Installations

Soil temperature was measured as a function of resistance. Fenwal JA33J1 resistance thermistors were soldered to lengths of general purpose speaker wire. Single wire and thermistor units were inserted in 1/4" O.D., 1/8" I.D. acrylic tubing and both ends of the tubing were sealed. The upper, exposed end was sealed with flexible silicone and the lower end was sealed with epoxy resin. Care was taken to minimize the occurrence of air bubbles in the epoxy. Excessive air close to the thermistor could produce a lag in the thermistor response to soil temperature changes. The magnitude of such a problem, should it occur, is unknown. It does represent a random experimental error, however, and attempts were made to reduce the chance of it occurring.

All resistance measurements were performed using a Beckman 330 multimeter precise to two decimal places. Several different meters were used over the course of the field season and both were checked to assure consistency between them.

A total of 38 thermistors were used in the study. Only one displayed any accumulation of moisture inside the acrylic tube, although the resistance measurements were not significantly altered. Comparison with observations by a 'dry' tube at the same site confirmed this. Several thermistors had to be repaired and one replaced due to damage caused by animals.

3.2.1.2 Thermistor Calibration

All thermistors were calibrated after the field season. Calibration was performed using a Lauda K-4/RD oil bath. Oil temperature in the bath was monitored with four platinum thermocouples. The average of the four thermocouple readings was used as the temperature for calibration, precise to two decimal places. All thermistors were calibrated over the range of resistances measured in the field.

The relationship between temperature and resistance may adequately be described by a semi-logarithmic equation. Resistances and temperatures for each individual thermistor were analysed using SPSS linear regression (Nie et al, 1975) in which values for resistance were logged. Of the 38 resulting equations none had R^2 values less than 0.9996. Maximum R^2 was 0.99992. The mean equation (mean values of a and b) is

$$Y = 49.5 \qquad - 48.5 \qquad \log x$$

where Y = soil temperature in ^{o}C

x = resistance in ohms (Ω)

This equation is plotted in Figure 3.5 along with those for ±1 standard deviation. Seventeen of the 38 thermistors had both slopes

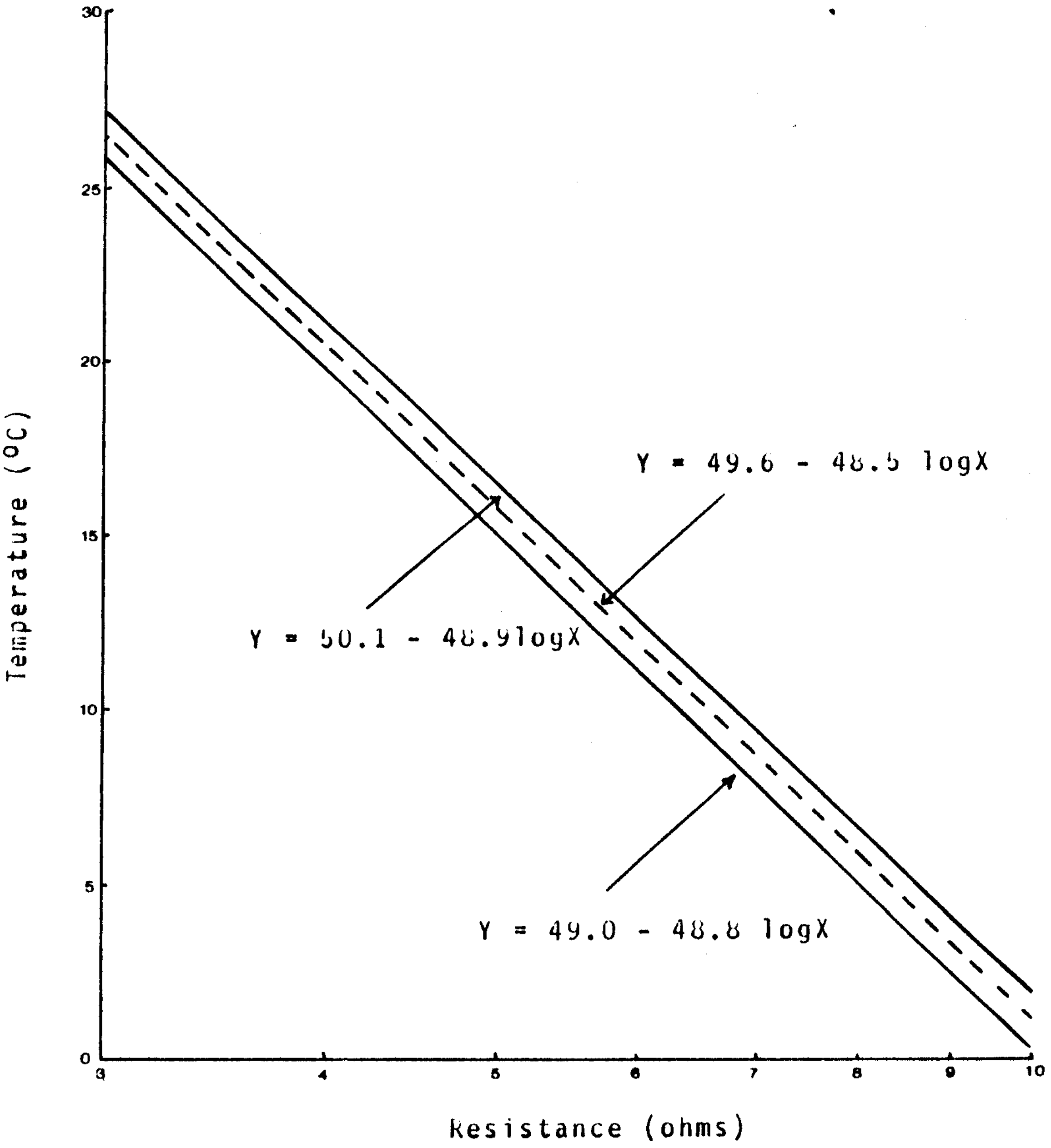

FIGURE 3.5 Mean (±1 S.D.) Equation derived from Thermistor Calibrations

and Y - intercepts in the ±1 S.D. range. Individual equations were used in calculating temperatures for further statistical analyses.

3.2.2 Soil CO_2

3.2.2.1 Field Installations

Method A: Lengths of stainless steel tubing (1/8" O.D., 1/16" I.D.) were inserted into the soil. The upper, exposed ends were capped with neoprene rubber septas (Pierce #12437) and sealed with flexible silicone. Prior to insertion into the soil 16 ga. wire was inserted into the tubes to assure the tubes were clear of soil down to the necessary depths. The wire was removed before the tubes were capped.

Samples of the soil atmosphere were taken by inserting one end of a double-ended vacutainer needle into the septa and then piercing a 3 ml. B-D evacuated glass tube (vacutainer) with the other end of the needle. After approximately ten seconds the vacutainer was pulled from the double-ended needle and then the needle was removed from the sampling tube. Prior to sampling by this procedure a volume of the soil atmosphere equal to the volume of the tube interior was removed using a glass syringe. This was done so that the collected sample would be representative of the soil atmosphere at that particular depth and time of sampling.

Method B: Soil CO_2 concentrations were measured 'on-site' using a Dräger gas detector pump, model 31, with a 100 cc draw and Dräger CH23501 CO_2 tubes. Samples were taken at depth in the soil using a set of nested stainless steel tubes designed and described by Miller (1981) and used also by Mills (1981). The apparatus works by drawing soil air from a specific depth up through the nested tubes and the Dräger tube into the pump where it is expelled. Depending upon the concentration of CO_2 in the soil air either 100 cc (1 stroke) or 500 cc (5 strokes) was withdrawn using the pump although the latter was more commonly required.

A volume of air, approximately 10 cc, is always present in the nested tubes and thus represents a volume of air of low concentration CO_2 which is always sampled along with the soil atmosphere. This particular systematic error is relatively insignificant compared to the possible errors in interpolating readings from the scale of the Dräger tubes. As well, small lateral variations in color reaction of the tube contents introduce an uncontrolable variation in scale readings.

By modifying the Miller-Dräger apparatus sub-samples could be taken of the soil atmosphere being measured with the Dräger tubes. These sub-samples were collected in the 3 ml vacutainers using the double-ended needle.

3.2.2.2 Laboratory Measurements of Vacutainer Samples

Samples of the soil atmosphere were stored until analysis in the vacutainers in which they were collected. Analysis of the samples was performed using a Beckman model 865 infrared gas analyser (IRGA) connected to a Rickadenki model B-281 chart recorder. Quite simply the IRGA works by comparing the difference in infrared energy absorption between a reference cell and a flow through cell which contains the sample. Nitrogen containing 210 ppm CO_2 was used as a carrier gas in the flow through cell.

Soil atmosphere samples were introduced into the IRGA through a sampling port. Removal of the sample from the vacutainers and injection into the IRGA was done with a 1.0 cc glass syringe. Each vacutainer was usually sub-sampled five times. Sub-samples were commonly 0.1 cc but in some cases were 0.15 cc. Before, during, and after each set of analyses numerous injections of calibration gases were made. The calibration gases used were Matheson certified standard CO_2 in air having CO_2 concentrations of 1500 ppm (±.15 ppm), 5120 ppm (±.512 ppm), and 9700 ppm (±1.94 ppm). By comparing the average peak height of each calibration gas with the maximum peak height of the sub-samples for any individual vacutainer, the relative concentration of CO_2 in each vacutainer could be calculated.

3.2.3 Sampling Design

At Rock Chapel soil temperature and soil CO_2 were measured under three distinctly different vegetation assemblages. The vegetation making up these assemblages can be adequately described as 1) mature deciduous forest, 2) rough scrub - presently regenerating to forest, and 3) uncut grass. In each assemblage duplicate sites were sampled. Soil temperature and CO_2 were measured at depths of 10 cm, 25 cm, and 50 cm at each of the six sites. Duplicate measurements of temperature were made for each depth at each site. This was done primarily as a check on individual thermistors. Soil CO_2 was measured once at each depth and site using the vacutainer method. A number of CO_2 measurements were also made within the vegetation assemblages using the Miller-Dräger apparatus.

At the other sampling sites (A, B, C, D and E on Figure 3.1) soil CO_2 was measured at depths of 10 cm and 25 cm using the Miller-Dräger apparatus. Vacutainer samples of the Dräger samples were also taken using the modified Miller-Dräger method.

CHAPTER 4

DATA DESCRIPTION, EVALUATION, AND ANALYSIS

4.1 Introduction

There are numerous techniques for collecting and/or measuring soil carbon dioxide. Generally these techniques may be grouped into those which determine concentrations of CO_2 and those which measure respiration rates. Of these the first group is more important in karst studies. The Dräger method has been used extensively in studies of soil CO_2 and cave air CO_2 (Miotke, 1974; James et al, 1975; James, 1977; Fritz et al, 1978; Gunn and Trudgill, 1982) but very little literature exists that attempts to determine the validity, or even the variability of the method. Likewise the vacutainer method, although somewhat more limited in use (Campbell, 1974; Reardon et al, 1979) has had very little testing done on the method itself.

The first portion of this chapter will review problems with the Dräger and vacutainer techniques. A number of tests for checking and cross-checking the methods with each other are described and the results given and discussed. The second portion of this chapter is devoted to the statistical analysis of the Rock Chapel soil temperature and CO_2 data. A model of CO_2 production is presented as a result of the statistical analysis.

4.2 The Dräger Method

4.2.1 Introduction

The measure of CO_2 Dräger tubes provide is a relative concentration. The amount of soil air required to produce a Dräger reading in the field is commonly 500 cc. Some tubes have several concentration scales and if CO_2 levels are great enough only 100 cc of soil air is required. However, unless volumetric pore space is calculated within a particular soil for which soil CO_2 has been measured, there is no way to estimate the volume of soil required to provide that volume of soil atmosphere. Furthermore for any single location the volume of soil required is variable. Soil moisture, in particular that caused by precipitation, controls the amount of pore space taken up by water. It can be hypothesized that a Dräger reading taken during relatively wet conditions would require a larger volume of soil than would a reading taken at the same place during relatively dry conditions, all other things being equal. Because of the variability in required soil volume, conditions under which CO_2 is produced will be variable. Therefore the relative concentration of CO_2 the Dräger provides is not necessarily a relative measure of exactly the same conditions (ignoring the variability of individual conditions) should repeated measures be made.

Because of the large air volume the Dräger requires, small soil CO_2 anomalies may not significantly affect the final measurement. Furthermore portions of the soil which require greater suction than the Dräger pump can produce in order to withdraw air from them may not contribute much, if any, CO_2 to percolating waters. As such it is not important that CO_2 in such portions, or 'elements' as they are referred to by Miller (1981), be measured. The problem remains, however, of a spatially and temporally variable soil volume required for Dräger measurements. Variability of pore space and size within a soil also affects the movement of CO_2 within the soil and between the soil and the atmosphere (Currie, 1970). These movements can affect CO_2 concentrations as well.

4.2.2 Evaluating the Dräger Tube

Using gases of known concentration CO_2 tests were performed to quantify the precision, accuracy, and reproducibility of results from the tubes. Two sets of tubes were used. The first had been stored in a freezer for a number of years and had passed their expiry day of April, 1979. The second set were new and had an expiry date of March, 1984. The tests were performed during February and March, 1982. The results of the tests are shown in Table 4.1.

As mentioned previously (section 3.2.2.1) there are several difficulties encountered when reading CO_2 percentages from Dräger tubes. The lack of a precise scale requires interpolation of values. CO_2 measurements made using the Dräger CH23501 tube and the 500 cc scale can be interpolated to approximately ±200 ppm. Furthermore some tubes display lateral variation in color change perhaps as a result of differential diffusion of CO_2 through the indicator material.

Beyond these difficulties the question of the accuracy and reproducibility of results from the tubes should be addressed. Two each of the old and new tubes were used to measure each gas. This was done to see if any variability between tubes was present. It is

Table 4.1 Comparison of Dräger tube readings with gases of known CO_2 concentration

Known Gas Concentration (ppm)	Old Tubes (expired April/79)		New Tubes (expired March/84)		Volume of gas tested
	Tube #1	Tube #2	Tube #1	Tube #2	
1500	800	800	800	800	500 cc
5120	3800	4000	4000	4000	500 cc
			5000	5000	100 cc
9700	8500	9000	8000	8000	500 cc
		5000	10,000	10,000	100 cc
51,900	45,000	47,000	55,000	56,000	100 cc

N.B. Only the 5120 ppm and 9700 ppm gases fall within a range that may be measured using both 100 cc and 500 cc scales.

important to discover if this variability exists since single measurements made in the field using Dräger tubes rely on one reading. With two of the calibration gases, 5120 ppm and 9700 ppm, readings were taken on both 100 cc and 500 cc scales of the same tube. The remaining two gases, 1500 ppm and 51900 ppm, have concentrations beyond the range in which this double-reading may be done.

In comparing readings for old and new tubes taken with similar volumes of air, it is apparent that in most cases little difference exists between expired and unexpired tubes. This suggests that storage at low, freezing, temperatures prolongs the usability of Dräger tubes three years or more beyond their expiry date. Several drawbacks are evident, however, when expired tubes are used. Old, expired tubes display more variation between tubes than do new, unexpired ones. Also, as the CO_2 concentration of the known gas increases, the variation in readings between old tubes increases. New tubes display no variation between readings except for the 51900 ppm gas.

All readings from old tubes indicate CO_2 levels less than the CO_2 concentrations they are measuring. Expired tubes, then, underestimate known gas concentrations. If this error were due to aging of the CO_2 absorbant in the Dräger tube, the tubes would overestimate known gas concentrations. As the absorbant loses its ability to absorb CO_2, a larger volume of absorbant would be required to indicate a given CO_2 concentration. This is obviously not the case according to the figures in Table 4.1. As such another explanation for underestimation must be offered. Perhaps the absorbant does not partially lose its ability to absorb CO_2, but rather the color redox indicator in the tubes (crystal violet) partially loses its ability to display the full extent of the absorption. New Dräger tubes display both underestimation and overestimation. Presumably, therefore, a different mechanism or set of mechanisms is responsible for the apparent non-random deviations from known concentrations in new tubes.

With respect to the new tubes the volume of gas sampled, either 500 cc or 100 cc, controls the accuracy of the Dräger reading to some extent. Readings taken with 100 cc samples (1 stroke) vary no more than 8% from the known concentration. Results of the 500 cc samples (5 strokes) vary at least 17.5% from the known concentration. It is interesting to note that the result of the 100 cc sample of 9700 ppm gas, using an old tube, was the farthest removed from reality (5000 ppm measured vs. 9700 ppm known). This suggests again that despite the similarity of most readings between old and new tubes, the age of the old tubes has affected their reliability.

It is difficult to ignore the systematic variation between 500 cc and 100 cc sample readings for the new tubes. Both 5120 ppm and 9700 ppm gases are underestimated 20% using 500 cc readings rather than 100 cc readings. For all new tubes larger samples were measured less accurately than smaller ones. These results were closely reproduced. It is evident that the CO_2 concentration of strokes two through five (the 101st through 500th cc of sample) are not indicated as they should be. A probable, simple explanation for this behaviour exists. As the first 100 cc of sample is drawn through the Dräger tube the CO_2 is absorbed and the extent of this absorption is displayed by a change in color of the redox indicator from white to purple. As the second, third, fourth and fifth 100 cc of sample are drawn through the tube they must pass through material which has already absorbed CO_2 from a previous stroke or strokes. If the chemical reaction is not complete after the first 100 cc slug of gas has passed through the absorbant, subsequent slugs of gas will try to complete the reaction in that portion of the tube. Thus, although there is no visual indication that the reaction in the colored portion of the tube is not complete, this is not evident in the color change of the reactant. The one stroke measurement of the 5120 ppm gas is 5000 ppm or 97.7% of what it should be. If each subsequent stroke is able to react with 97.7% of what is left from previous strokes the end result is still 97.7% of 5120 ppm. Some other mechanism then is causing an increasing reduction in the amount of reaction so that after five strokes the Dräger indicates only 4000 ppm, or 78.1% of what it should be.

Considering the non-systematic order in which these measurements were made, it is improbable that trends described here are due to differential withdrawal of CO_2 or air from the calibration gas cylinders. Neither does the rate of gas flow from the cylinders affect the Dräger reading, speed of operation, or quality of color in the redox indicator.

4.2.3 Effect of soil Texture on Dräger CO_2 Measurements

Using a soil map (Presant et al, 1965) different soil textures within Hamilton-Wentworth were located. Only five different textures of soil exist in the region although numerous replications of these textures exist. Each texture nearest, and in one case within, Rock

Chapel Sanctuary were sampled for CO_2 using the modified Miller-Dräger apparatus. Readings were taken at 10 cm and 25 cm depth. Vacutainer subsamples from each 100 cc volume of soil air were also taken.

The location of the texture sites is shown in Figure 3.1. The soil and topographic characteristics of each site are given in Table 3.1. The results of the Dräger measurements are given in Table 4.2. All measurements were made with old tubes (because new tubes were not available at the time) over a two day period at the end of October, 1981. Both days were similar with respect to temperature and time of sampling. A heavy rain (18.0 mm) had fallen three days prior to the first days measurement.

It would appear that some relationship exists between soil texture and the Dräger CO_2 measurements for those textures. CO_2 concentrations do seem to increase with a decrease in the coarseness of the soil texture especially at a depth of 25 cm. In view of the problems of variability and underestimation mentioned in the previous section, this trend should not be regarded as a conclusive one.

In all five soils 25 cm readings are equal to or greater than 10 cm readings. Because of the similarity of 10 cm and 25 cm readings for gravelly loam and sandy loam textures, an apparent CO_2 increase with depth may be due to tube to tube variability. The three finer textured soils, however, have sufficiently large differences between 10 cm and 25 cm concentrations that tube to tube variability would not alter such a trend. At 25 cm depth the difference in CO_2 concentrations between loam and silty loam soils is so small it would be fallacious to suggest it is a result of a difference in texture. Between

Table 4.2 Dräger readings taken in various soil textures.

Relative Texture	Soil Texture (Location)		CO_2 Concentration (in ppm)	
			10 cm	25 cm
Coarse	Gravelly loam	(C)	5000	5000
	Sandy loam	(B)	1600	2400
	Loam	(E)	5000	9000
	Silty loam	(D)	5000	10,000
Fine	Silty clay loam	(A)	12,500	18,000 (100 cc)

N.B. All readings required 500 cc except where noted.

sandy loam, loam-silty loam, and silty clay loam soils, however, the variation in concentrations at 25 cm are large enough that tube to tube variability would not mask a textural effect on CO_2 values.

What mechanisms then, could be responsible for CO_2 concentrations to increase as soil texture becomes finer? The physical differences between individual soils as represented by texture is not solely responsible for CO_2 variations. The response of soil moisture and various biological processes to a range of environments as dictated by texture may be more important. Finer textured soils probably hold more moisture and hold it longer than do coarse textured soils. Rose (1979) quotes available water capacity values for soils of different textures, as measured by Salter and Williams (1965), which support such a generalization. The presence of increased moisture, then, may support or promote the production of CO_2. Under drier conditions, in coarser soils that drain relatively quickly and are relatively well ventilated, CO_2 that is produced may diffuse through the soil to the atmosphere more quickly than in moister conditions. Furthermore finer textured soils, because of their relatively poorer ventilation may experience some accumulation of CO_2 which could account for elevated concentrations. Higher concentrations at greater depth in the soil may also be accounted for by CO_2 accumulating in this manner. Van Bavel (1951), in a study of soil aeration by diffusion, states that gaseous movement (diffusion) is not a soil characteristic but is controlled by porosity and porosity is determined by moisture content and compaction.

4.2.4 Some General Conclusions Regarding CO_2 Measurements with the Dräger

Measuring CO_2 with a Drager pump and tubes is quick and relatively inexpensive compared to alternative methods requiring gas analysers, calibration gases and technicians. It is also extremely portable and provides immediate on site measurements. For these reasons the Dräger method is valuable. The accuracy of Dräger tubes, especially when 500 cc samples are taken, is not entirely reliable. It does provide a researcher with some idea of the range and variability of CO_2 levels that exist at a location. For measurements that are relied upon for personal safety, such as in foul air caves (James et al, 1975; James, 1977) or mines, reliance upon Dräger tubes may be somewhat more tenuous.

4.3 The Vacutainer - IRGA Method

4.3.1 Introduction

Determining the amount of CO_2 in samples collected in vacutainers provides a relative concentration for those samples. The use of vacutainers to collect soil air samples requires only 3 ml of the soil atmosphere. This is a relatively small volume compared to that required by the Dräger (100-500 cc). As well, the volume of soil needed to provide a vacutainer sample will be much smaller. There still remains the problem of a variable soil volume during repeated sampling, although with vacutainers it occurs on a much smaller scale than with the Dräger apparatus.

Because of the small volume required to fill the vacutainer, the placement of semi-permanent sampling sites may be critical. Should the stainless steel tube, through which the sample is drawn, be driven into a zone of anomalous CO_2 concentration, the sample may not be representative of the soil atmosphere at that depth. To ascertain if CO_2 measurements at a particular location are a result of small scale anomalies is a problem that is beyond the scope and purpose of this study. Such a problem would require an intensive micromorphological examination of the soil and its biologic processes.

The vacutainer itself is used simply as a sterile storage vessel. The processes of getting the soil air sample into the vacutainer for storage, and out of the vacutainer for analysis, should not be susceptible to variation of technique and thus to possible error. To this end the double-ended needle and glass syringe were used consistently throughout the study in the most efficient manner possible - that which reduces the transferring of the sample to a minimum.

The final step of the vacutainer method, sample analysis with the IRGA, is undoubtedly the most frustrating. Despite care being taken through consistent field sampling and storage, variation between subsamples of a vacutainer sample was evident. It is suspected that such variation is partially due to a pressure reduction in the vacutainer through sub-sample withdrawal. This problem as well as an analysis of vacutainer storage potential are discussed in following sections.

4.3.2 Vacutainer Behaviour and Characteristics

4.3.2.1 Accuracy and Sample Transfer Capability

To determine the accuracy and sample transfer capability of vacutainers a number of them were filled with a gas of known concentration CO_2 and were then immediately analysed with the IRGA. The pressure to which the vacutainers were filled was varied to determine how this affected measurement as well. This testing was done on three days over a period of one week so as to reduce the chance of systematic errors occurring as a result of operator bias. The results of these analyses are shown in Table 4.3.

It is obvious that the vacutainers analysed on day 1 show an increase in calculated concentration as the pressure to which the vacutainer was filled increases. Although the real concentration of gas in these vacutainers was the same, the mass of gas in each vacutainer varied as a result of pressure differences. Because the IRGA is sensitive to mass variations the concentrations apparently vary in the first day's analyses. (This problem is discussed further in section 4.3.2.3.) In the second and third days' analyses the calculated concentrations still vary but only on the order of about 200 ppm. Day 1 analyses varied 750 ppm. Since the vacutainers analysed in days 2 and 3 were filled to approximately the same pressure, the variation they display is partially a result of the variability of the IRGA and partially a result of differences in the vacutainers themselves. Very slight differences in the pressure to which the vacutainers were filled must also cause some variation in the calculated concentration. Vacutainer samples in the field

Table 4.3 Results of IRGA analysis of vacutainers filled with a known gas concentration.

Day	Vacutainer	Calculated Concentration (ppm)	% Of Known Concentration (9700 ppm)
1	1^A	8690	89.6
	2^B	9090	93.7
	3^C	9440	97.3
2	1^B	9070	93.5
	2^B	8930	92.1
3	1^A	8790	90.6
	2^A	8980	92.6
			$\bar{x}$ = 92.8

A - filled to approximately atmospheric pressure

B - filled to slightly greater than atmospheric pressure

C - filled to much greater than atmospheric pressure are probably filled to a pressure slightly less than or equal to atmospheric.

The accuracy of vacutainers with respect to their capability to transfer a gas of known concentration is comparable to the accuracy of new Dräger tubes for measuring the same known gas. Overall the vacutainers in Table 4.3 retained 92.8% of the known concentration (9700 ppm). New Dräger tubes measured 82.5% of the same known concentration for a 500 cc sample, and 103.1% from a 100 cc sample (Table 4.1). It is unlikely that vacutainers, under any pressure, could retain 100% of the known concentration using the equipment in this study. Under very high pressures, vacutainers will pop their tops.

4.3.2.2 Long Term Storage Capability

Relatively long term storage capabilities of vacutainers have been studied previously (Bunting and Campbell, 1975). For this study a number of vacutainers were filled with a gas of known concentration (9700 ppm) and were stored. Storage was at room temperature and the vacutainers were kept covered at all times. At several nearly random intervals two or more of the vacutainers were analysed with the IRGA. The results are given in Table 4.4.

Same day analysis of several filled vacutainers as well as those stored 82 days were made during the same IRGA run. The calculated concentrations of the vacutainers analysed right after filling, as in the previous section, were much lower than any previously analysed (67% retained, n = 2 vs. 92.8% retained, n = 7). This fact, coupled with several technical problems encountered with the IRGA

Table 4.4 Results of IRGA analysis of vacutainers filled with a known gas concentration and stored for 2, 5, and 82 days.

Elapsed Time (Days)	Vacutainer	Calculated Concentration (ppm)	% Of Known Concentration (9700 ppm)
2	1	8111	83.6
	2	7792	80.3
	3^{C}	8522	87.9
	4^{C}	8842	91.2
5	1	7722	79.6
	2	7988	82.3
82	1	6611	68.2
	2	6097	62.9

C - filled to much greater than atmospheric pressure during the run do not inspire confidence in the results of the vacutainers stored 82 days. It is possible that these particular calculated concentrations are lower than they should be.

Two of the vacutainers analysed after two days elapsed time were filled to a pressure much greater than atmospheric. Like those in the previous section, the pressure filled vacutainers yielded the highest calculated concentrations, while those that were not pressure filled yielded lower calculated concentrations.

In general, the calculated concentrations of the vacutainers decreases as the elapsed time increases. Diffusion of some sort must be taking place between the vacutainer and the atmosphere to account for this. In the previous section it was determined that about 90-92% of the known concentration is retained in same day analyses. After a period of two days, without extreme pressure filling, about 82% is retained and after five days slightly less than 82%. Ignoring the 82 day data it appears that after an initial loss of about 10% for same day analyses, and a subsequent loss of 10% after two days, the calculated concentration does not decrease as markedly for storage periods up to five days. A more consistent and frequent sampling interval, and analyses of greater numbers of vacutainers would be necessary to forward further conclusions along this line.

4.3.2.3 Pressure Reduction Characteristics

Air expands and contracts to fill any available volume. This concept is not unknown in science. If some portion of air is removed from a container of fixed volume, the remaining air will still occupy

100% of that volume, however the pressure will be reduced in the container. Assuming a homogenous mixture exists the relative concentrations of the various components of air remains the same in the container even though portions of it are removed. The mass of the components of air, CO_2 being one of them, decreases as portions of air are removed from the container. This simplification of volume, mass, and concentration may be applied to the action of withdrawing sub-samples from vacutainers.

The IRGA recognizes variations in the mass and concentration of CO_2 in a sample. Theoretically successive sub-samples taken from the same vacutainer and analysed with the IRGA should show a progressive decrease in peak heights on the recorder for each additional sub-sample. This is expected because the mass of the sample in the vacutainer is reduced as each sub-sample is withdrawn. Unfortunately this theoretical behaviour is not reflected in the actual behaviour of vacutainer sub-samples analysed with the IRGA. More than 270 vacutainer samples were taken in the field. The majority of these, 72%, displayed a pattern of peak heights not unlike that shown in Figure 4.1. This pattern is a composite of 16 vacutainers. Ten sub-samples were withdrawn from each vacutainer and in Figure 4.1 are represented in their order of withdrawal. Obviously the first sub-sample does not have the greatest value. It is, in fact, comparable with the 8th sub-sample. The third sub-sample usually has the greatest value.

Why this pattern exists rather than the theoretical one described at the beginning of this section, is not fully understood. From reviewing the total data set it appears that samples having

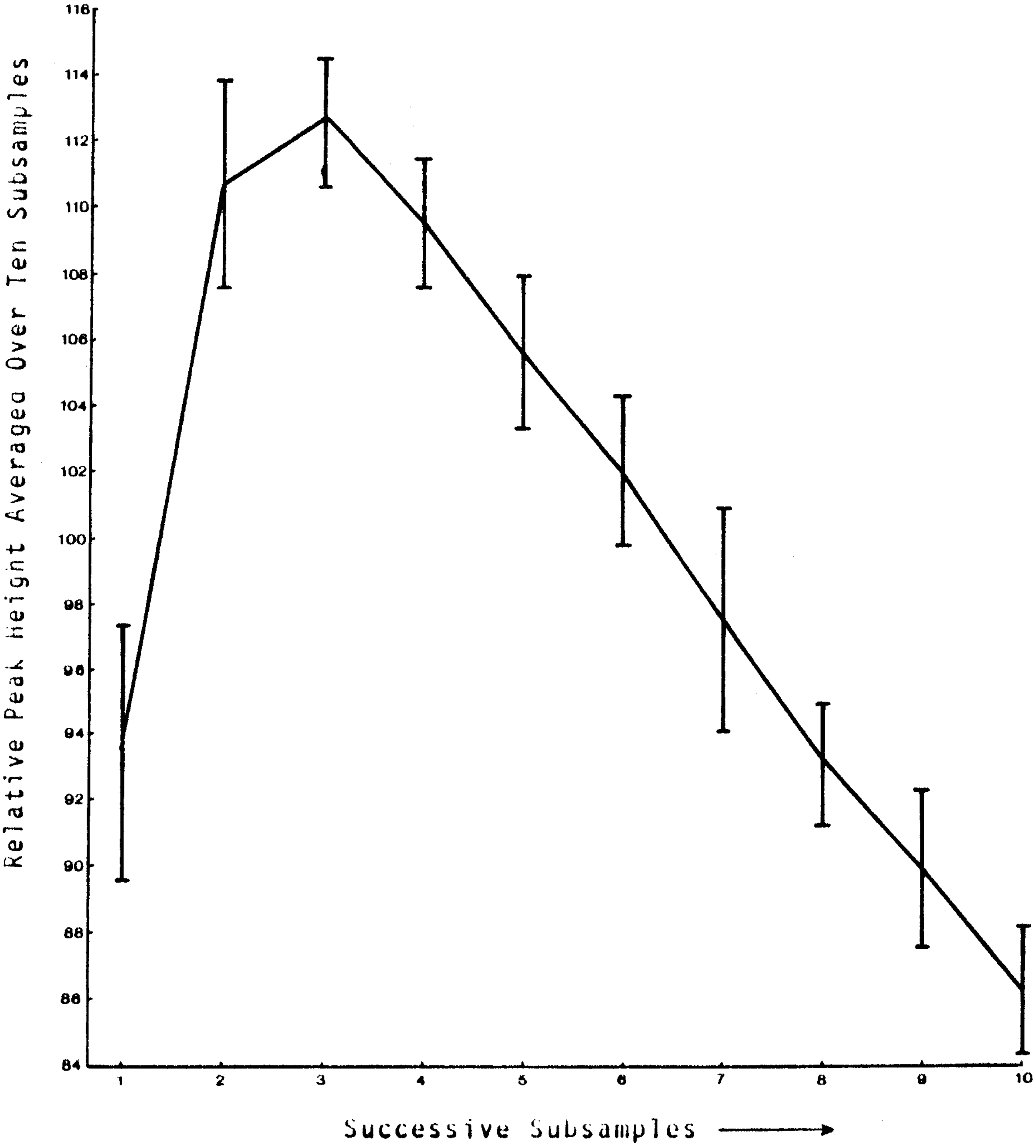

FIGURE 4.1 Relative CO_2 Concentrations of Successive Subsamples Withdrawn from Vacutainers

relatively low calculated concentrations have a tendency to follow the theoretical pattern although this does not occur consistently throughout the data set. This observation is complicated by the fact that the IRGA displays a 'memory' effect. That is, if a sample having a relatively high calculated or known concentration is injected into the IRGA the next sample that is injected appears abnormally high. This may be a result of incomplete purging of the system by the carrier gas.

An attempt was made to reproduce the pattern shown in Figure 4.1 using vacutainers filled in the laboratory with a gas of known concentration. By reproducing the behaviour of field samples it was thought that the pattern could be mathematically modelled and corrected for the consistently low first sub-sample. Sub-samples 3 through 10 (Figure 4.1) indicate a relatively consistent decrease in value; a pattern similar to the theoretical one described earlier. Unfortunately vacutainers filled in the laboratory did not behave like those containing samples from the field. Less than 39% (5 of 13) of the lab filled vacutainers behaved like the majority of those from the field.

Why the first sub-sample should be as low as it is in the majority of cases is unknown. Also why the lab filled vacutainers did not duplicate the pattern of the others is unknown athough it is suspected to be due to the filling technique. Further speculation would be dangerous.

4.3.3 Conclusions

The IRGA system is undoubtedly responsible for far less error than that created by the vacutainers and the procedures associated with them in this study. As such, several modifications to the vacutainer technique are proposed. First, rather than taking five or more replicate sub-samples from each vacutainer, a single large sample, perhaps 2 ml, should be used. Duplicate vacutainer samples could be taken in the field. Only 6 ml (2 x 3 ml) of the soil atmosphere would be required to do this, and the two calculated concentrations would not have been subject to the problems of pressure reduction through multiple withdrawals. However, the problem of a low, variable first sample, as in Figure 4.1, still exists. Samples in the field should be analysed as quickly as possible although it may be feasible to develop a variable correction factor for vacutainers stored longer periods. Finally, the change in sample temperature from the field to the laboratory may alter the calculated concentrations.

The main advantage of the vacutainer-IRGA method is that is requires a small soil atmosphere sample, compared to the Dräger. Permanent sampling stations, once installed, do not alter the soil structure whereas the Miller-Dräger apparatus must be shoved into the soil and removed whenever a single sample is taken. If an IRGA, or gas chromatograph, is available the vacutainer method is probably as inexpensive as sampling with Dräger tubes.

4.4 IRGA Analysis of Dräger Samples

A number of vacutainer samples were taken of the soil atmosphere using the modified Miller-Dräger apparatus (section 3.2.2.1). The purpose of collecting and analysing such samples is to compare

CO_2 concentrations as measured by the Dräger with IRGA measurement of the same air. Furthermore by taking vacutainer samples after each successive Dräger stroke, the variation in concentration of the air the Dräger is measuring can be determined. The results of these analyses are given in Table 4.5. Measurements were made on five different days. Those on September 28 and October 8 are from Rock Chapel. The remainder were made during Dräger measurements of CO_2 in soils of different textures (section 4.2.3). The data for September 28 includes IRGA analyses of Dräger air taken only after the fifth stroke, All other data include calculated concentrations by the IRGA after each Dräger stroke.

There is no obvious pattern to the variation found in the IRGA calculated concentrations for successive strokes. No evidence exists that the successive withdrawal of relatively large volumes of soil air, as with the Dräger, differentially removes air containing high or low concentrations of CO_2. Some samples have relatively high concentrations in the first stroke, notably To-10 and An-25. Other samples have the lowest concentration during the first stroke (Fl-10 and Gi-25). Still others have concentrations in the first stroke that are neither the highest or lowest of those measured (An-10 and Fl-25). The fact that variation exists throughout all strokes of all samples suggests that the withdrawal of CO_2 from the soil is not particularly controlled by the ease of air movement within the soil. However, the air within the soil is not entirely homogenous either, thus stroke to stroke variations exist as measured by the IRGA.

Differences exist between the average calculated concentration

Table 4.5 A comparison of Dräger measurements with IRGA analyses of vacutainer samples taken of the Dräger air.

Date	Site	CO_2 Concentration (% Volume)		Site	CO_2 Concentration (% Volume)	
		Vacutainer-IRGA	Dräger		Vacutainer-IRGA	Dräger
Sept.28*	G-10	.46	.45	G-25	.39	.55
	S-10	.49	.44	S-25	.20	.10
	F-10	.44	.40	G-25	.42	.50
Oct. 8	G-10 #1**	.35		G-25 #1	.33	
	#2	.32		#2	.25	
	#3	.31	.29	#3	.28	.20
	#4	.29		#4	.27	
	#5	.28		#5	.23	
Oct.29	To-10 #1	.73				
	#2	.65				
	#3	.71	1.50			
	#4	.73				
	#5	.78				
Oct.30	Fl-10 #1	.32		Fl-25 #1	.52	
	#2	.37		#2	.55	
	#3	.37	.50	#3	.49	.90
	#4	.34		#4	.53	
	#5	.37		#5	.50	
	Gi-10 #1	.21		Gi-25 #1	.21	
	#2	.19		#2	.25	
	#3	.20	.16	#3	.24	.24
	#4	.21		#4	.24	
	#5	.21		#5	.23	

... continued

Table 4.5 A comparison of Drager measurements with IRGA analyses of vacutainer samples taken of the Dräger air (continued).

Date	Site	CO_2 Concentration (% Volume)		Site	CO_2 Concentration (% Volume)	
		Vacutainer-IRGA	Dräger		Vacutainer-IRGA	Dräger
Oct.30 (cont'd.)	Dk-10 #1	.30	.50	Dk-25 #1	.26	.50
	#2	.37		#2	.29	
	#3	.33		#3	.29	
	#4	.36		#4	.32	
	#5	-		#5	.27	
Oct.31	To-10 #1	.77	1.25	To-25 #1	.88	1.80
	#2	.58		#2	.76	
	#3	.60		#3	.74	
	#4	.59		#4	.80	
	#5	.55		#5	.78	
	An-10 #1	.34	.50	An-25 #1	.61	1.00
	#2	.32		#2	.53	
	#3	.35		#3	.50	
	#4	.36		#4	.32	
	#5	.33		#5	.50	

* Vacutainer sample taken only after 5th Dräger stroke.

** #'s 1 to 5 indicate vacutainer sampling after each successive Dräger stroke.

for each sample location and the measurement made by the Dräger. Generally, the lower the concentration the smaller the absolute difference between IRGA and Dräger concentrations. Also for all measurements made at 10 cm and 25 cm depth at a single location, the 10 cm concentrations show smaller differences between IRGA and Dräger methods than do the 25 cm concentrations. These observations suggest that vacutainers may be less capable of storing air with relatively high CO_2 concentrations than air with relatively low concentrations. Since all field samples are taken using the vacuum of the vacutainer they cannot be filled to pressures greater than those that are found in the soil environment. Should the pressure vary between 10 cm and 25 cm depth in the soil, exchange between vacutainers and the atmosphere may take place during storage according to the internal vacutainer pressure at the time of sampling.

4.5 Dräger vs. Vacutainer-IRGA Measurements at Rock Chapel

A number of Dräger measurements (old tubes) were taken at Rock Chapel. Some were co-incident with vacutainer sampling and soil temperature measurements. Co-incident measurements (IRGA and Dräger) were taken on four dates and Dräger measurements only were taken on two others. A comparison of Dräger measurements with those determined by IRGA analysis of vacutainer samples is made in Table 4.6. All Dräger measurements were taken between duplicate sites (I and II) within vegetation types (forest (F); scrub (S), grass (G)). The majority of Drager measurements are from the grass site.

An examination of the data in Table 4.6, specifically the

Table 4.6 Dräger measurements taken at Rock Chapel compared to co-incident vacutainer-IRGA measurements.

Date	Site	CO$_2$ Concentration (% Volume)			
		Dräger (# of Strokes)		Vacutainer-IRGA	
				Site I	Site II
Aug. 28	G-10	.10 (10)		-	.14
	G-25	.35 (10)		.31	.50
	S-10	.20 (10)		.23	.17
	S-25	.37 (10)		.35	.15
Sept. 1	G-10	.22			
	G-25	.58			
	S-10	.38			
	S-25	.82	.5(1)		
	F-10	.43			
	F-25	1.25	.8(1)	data not collected	
Sept.15	G-10	.40			
	G-25	1.10			
	S-10	.40			
	S-25	1.40			
Sept.28	G-10	.45		.18	.22
	G-25	.55	.75(1)	.16	.80
	S-10	.44		.47	.18
	S-25	.10		.71	.64
	F-10	.40		.29	.32
	F-25	.50		-	.56
Oct. 8	G-10	.29		.17	.20
	G-25	.20		.35	.75
Nov. 23	G-10	.11		.14	.33
	G-25	.15		.19	.50

N.B. # of strokes equal 5 unless otherwise indicated.

CO_2 concentrations for sites I and II, shows that readings taken under grass (G) are always higher for site II than for site I. Under scrub (S) all site I measurements are higher than site II. These two trends do not occur throughout the total data set (July-December). The difference in Dräger measurements between vegetation types cannot be a result of textural differences in the soils at Rock Chapel. From Table 3.1 it can be seen that three soil types are found at Rock Chapel, but they all have the same texture (loam).

The Dräger readings indicate that on any of the given dates (Table 4.6) there appear to be CO_2 variations between vegetation types and between depths. Vacutainer-IRGA measurements also display noticeable variability between depths. Vegetational differences are difficult to postulate because data from all vegetation types exists on one day only (September 28). From a comparison of co-incident Dräger-IRGA measurements it is evident that large discrepancies exist, in particular on September 28 at S-25. At this time and location a Dräger tube measured 0.10% CO_2 between sites I and II while at those sites the concentration was .71% and .64% respectively. Data also exist where IRGA measurements are lower for sites I and II than for the Dräger reading taken between sites (September 28, G-10). The variation between sites I and II may be due to measurable differences in CO_2 concentration, or they may be the result of mis-handling at some point in sample collection, storage, or analysis. On the basis of these observations it is difficult to arrive at conclusions regarding this particular data set. As such a series of analysis of variance (ANOVA) tests was performed to determine if any of the types of measurement allows a distinction to be made between vegetation types and/or depths from the CO_2 data.

BMDP Biomedical Computer Programs, P-Series (Dixon and Brown, 1977) were used to evaluate the data in Table 4.5. Using ANOVA testing (BMDP2V) the data were analysed three ways. First, within a vegetation type (grass) different measures of CO_2 were compared to see if significant variations between 10 cm and 25 cm depths was present. Four types of CO_2 measures were used; Dräger measurements, site I measurements, site II measurements, and the average of site I and II measurements. This first series of analyses were performed using data from August 28, September 28, October 8 and November 23. Secondly, for a single day - September 28, the four CO_2 measures were analysed to determine if significant variation between vegetation types and/or between depths was evident. Finally, Dräger measurements from September 1 were tested and compared to results from September 28. The results of these three sets of analyses are given in Tables 4.7, 4.8, and 4.9.

In the first set of analyses the hypothesis being tested is that for each type of measurement CO_2 variations are not a result of differences in depth. Alternatively the null hypothesis states that differences exist between 10 cm and 25 cm depths as reflected by variations in CO_2. The results of the ANOVA tests (Table 4.7) indicate that variance due to the depth factor is insignificant (tail probability > 0.0500) for Dräger measurements and IRGA analysis of site I samples. However, the measurements made at site II and the average of site I and II values display significant variations due to depth. The fact that Dräger and site I measures do not show significant variation may

Table 4.7 Results of ANOVA Tests on Different CO_2 Measures for Aug. 28, Sept. 28, Oct. 8, Nov. 23; Sites G-10, and G-25 Only.

CO_2 Measure	Source Of Variance	Sum Of Squares	D.F.	Mean Square	F	Tail Probability
Dräger	Mean	.6050	1	.6050	20.17	.0041*
	Depth (Between Groups)	.0113	1	.0113	.38	.5627
	Error (Within Groups)	.1780	6	.0300	-	-
IRGA-Site I	Mean	.3362	1	.3362	75.98	.0001*
	Depth	.0181	1	.0181	4.08	.0899
	Error	.0266	6	.0044	-	-
IRGA-Site II	Mean	1.4792	1	1.4792	92.69	.0001*
	Depth	.3445	1	.3445	21.58	.0035*
	Error	.0958	6	.0160	-	-
Mean IRGA (Site I + Site II/2)	Mean	.7938	1	.7938	161.18	.0000*
	Depth	.1301	1	.1301	26.41	.0021*
	Error	.0296	6	.0049	-	-

N.B. *'s indicate significance at a 95% level of confidence.

Table 4.8 Results of ANOVA Tests on Different CO_2 Measures for September 28, F-10, F-25, S-10, S-25, G-10, G-25.

CO_2 Measure	Source Of Variance	Sum Of Squares	D.F.	Mean Square	F	Tail Probability
Dräger	Mean	.9923	1	.9923	30.75	.0310*
	Vegetation	.0585	2	.0293	.91	.5244
	Depth	.0033	1	.0033	.10	.7805
	Error	.0645	2	.0323	-	-
IRGA-Site I	Mean	.9361	1	.9361	73.62	.0133*
	Vegetation	.1791	2	.0900	7.04	.1243
	Depth	.0400	1	.0400	3.15	.2181
	Error	.0254	2	.0127	-	-
IRGA-Site II	Mean	1.2331	1	1.2331	82.94	.0118*
	Vegetation	.0105	2	.0053	.35	.7384
	Depth	.2731	1	.2731	18.37	.0504
	Error	.0297	2	.0149	-	-
Mean IRGA (Site I + Site II/2)	Mean	1.0668	1	1.0668	955.36	.0010*
	Vegetation	.0242	2	.0121	10.85	.0844
	Depth	.1320	1	.1320	118.22	.0084*
	Error	.0022	2	.0011	-	-

N.B. *'s indicate significance at a 95% level of confidence

Table 4.9 Results of ANOVA Tests of Dräger Measurements on September 1 and 28, sites F-10, F-25, S-10, S-25, G-10, G-25.

Date	Source Of Variance	Sum Of Squares	D.F.	Mean Square	F	Tail Probability
Sept. 1	Mean	2.2571	1	2.2571	74.74	.0131*
	Vegetation	.1941	2	.0971	3.21	.2373
	Depth	.4374	1	.4374	14.48	.0626
	Error	.0604	2	.0302	-	-
Sept. 28	Mean	.9923	1	.9923	30.75	.0310*
(From Table 4.5)	Vegetation	.0585	2	.0293	.91	.5244
	Depth	.0033	1	.0033	.10	.7805
	Error	.0645	2	.0323	-	-

N.B. *'s indicate significance at a 95% level of confidence

be a reflection of the inaccuracy of the Dräger readings or of an error in the vacutainer-IRGA method. Although site II results are significant while those for site I are not, and although differences between CO_2 measurements at both sites may exist, statistically significant differences between sites I and II do not necessarily exist.

The second set of analyses, for September 28, includes a vegetation factor as well as a depth factor. The hypothesis tested is that no significant variation exists as a result of differences in vegetation or depth. The results (Table 4.8) show that of the four methods analysed, none display significant variation due to vegetation differences. Furthermore, only the average of sites I and II (Mean IRGA) shows significant variation due to depth. The significant variation with depth found in the first analysis of site II (Table 4.7) is not found when the vegetation factor, however insignificant it may be, is introduced (Table 4.8). The fact that significant variation with depth is not found in the second analysis (Table 4.8) may be because the depth variation is less meaningful given that vegetation differences exist. The second analysis is also based on a signle day's data rather than on four days as in the first analysis. This may also influence the results.

Finally, the results of the third analysis (Table 4.9) show September 1 Drager measurements to be much the same as September 28 Dräger measurements. Significant variation cannot be attributed to differences in either vegetation or depth. ANOVA testing of September 28 Mean IRGA data shows a significant depth effect. That the Dräger measurements for the same data and site locations cannot, suggests that the old tubes are incapable of accurately displaying areal variations in CO_2.

In general it can be concluded from comparing Drager and vacutainer-IRGA methods of measurement that variations in CO_2 due to changes in depth are present but are not detectable by the Drager method or even by the supposedly duplicate sites I and II. Differences in site I and II values (Table 4.6) suggests a CO_2 gradient exists between them. It also appears that CO_2 concentrations increase with depth. This is supported by ANOVA testing of the average of site I and II readings which always show significant variation due to changes in depth. That site I and II samples do not display significant variations with depth while the average of their values do, implies that the CO_2 concentrations vary from point to point while having similar depth and vegetation cover. The necessity of taking duplicate samples is made apparent as a result of this. The Drager measurements, which are taken approximately mid-way between sites I and II, should be comparable with the average of site I and II readings. It is obvious, however, that they are not.

4.6 The Behaviour of Soil Temperature and CO_2 and the Rock Chapel CO_2 Model

4.6.1 Introduction

The development of a predictive model of soil CO_2 based on soil temperature and vegetation and depth differences, was one of the objectives of this study. Secondary to this objective was the determination of the effect of vegetation and depth of CO_2 concentrations in the soil. Do differences in CO_2 occur as a result of the vegetation being forest, scrub, or grass? Are the differences, should they exist, significant? Also, are variations in CO_2 concentrations with depth significant?

Finally, how meaningful is soil temperature as a predictor of soil CO_2? Before describing the model, a qualitative analysis and evaluation of the behaviour of soil temperature and soil CO_2 will be made.

4.6.2 The Behaviour of Soil Temperature at Rock Chapel

It will be assumed in this discussion that the behaviour of soil temperature is attributable only to differences in vegetation between sites. Climatic differences between sites are therefore assumed to be non-existant. These are valid assumptions because the forest, scrub, and grass sites are within several hundred meters of each other. Furthermore all sites have similar aspects and slopes. Figures 4.2, 4.3 and 4.4 show the mean soil temperature for the sites at depths of 10 cm, 25 cm, and 50 cm. Each data point is a mean of four measured temperatures; two for each of duplicate sites I and II.

In general the temperatures under each vegetation type display a similar seasonal pattern of variation. Temperatures are high during the summer and early fall and then decrease in late fall and early winter. Soil temperatures measured under the forest display the lowest temperatures for all three depths. The average temperature for all dates for individual depths show that the soil temperature decreases from 10 cm to 25 cm to 50 cm under the forest cover. Temperatures under the scrub cover are higher than either forest or grass at 10 cm depth. At 25 and 50 cm depths, however, the grass site displays the highest temperatures. Scrub temperatures are only marginally lower than those for grass at 25 cm and 50 cm depths. These differences are a result of the vegetation cover. Forest temperatures are lowest

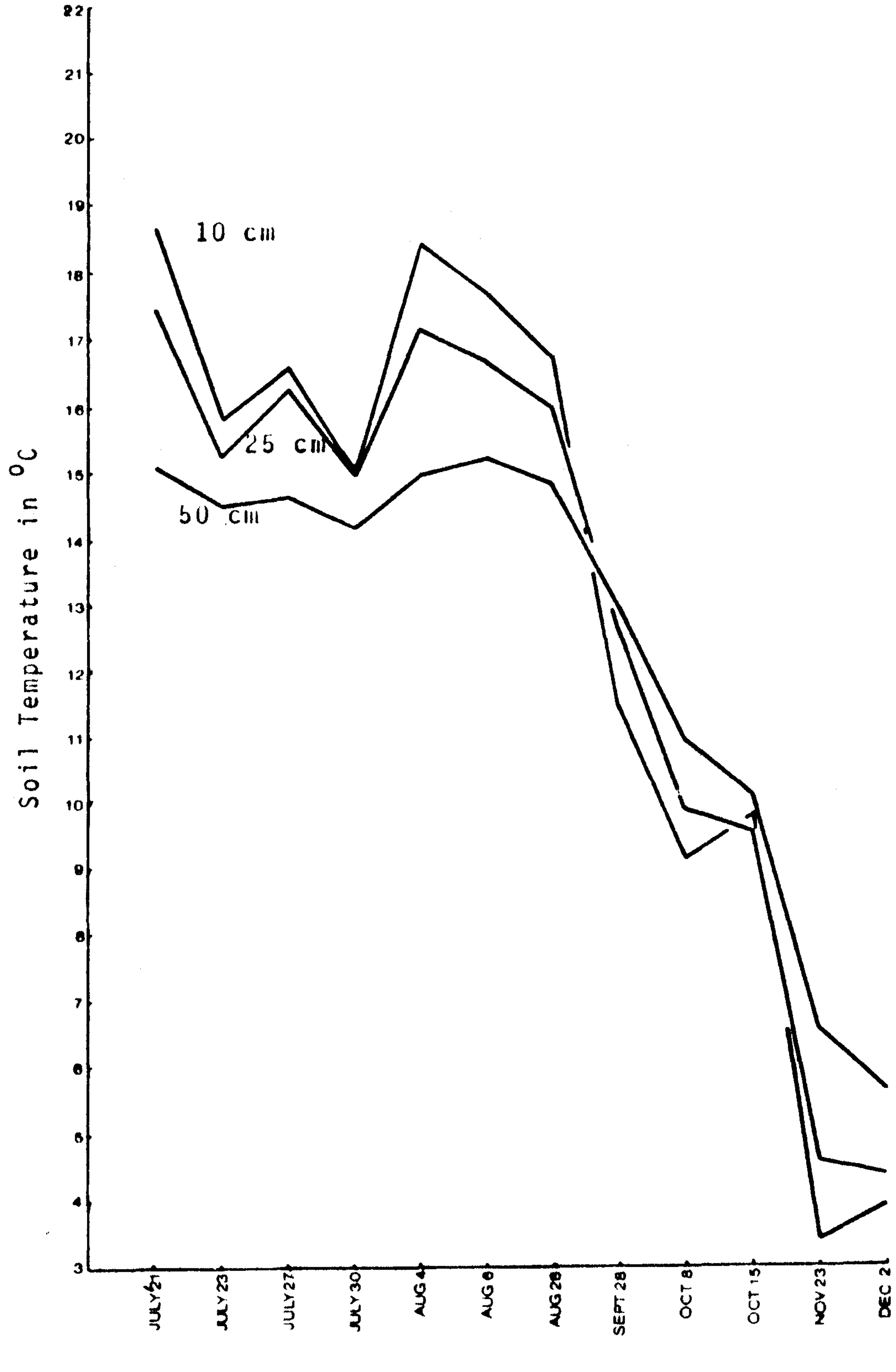

FIGURE 4.2 Mean Temperature for Forest (F) Sites

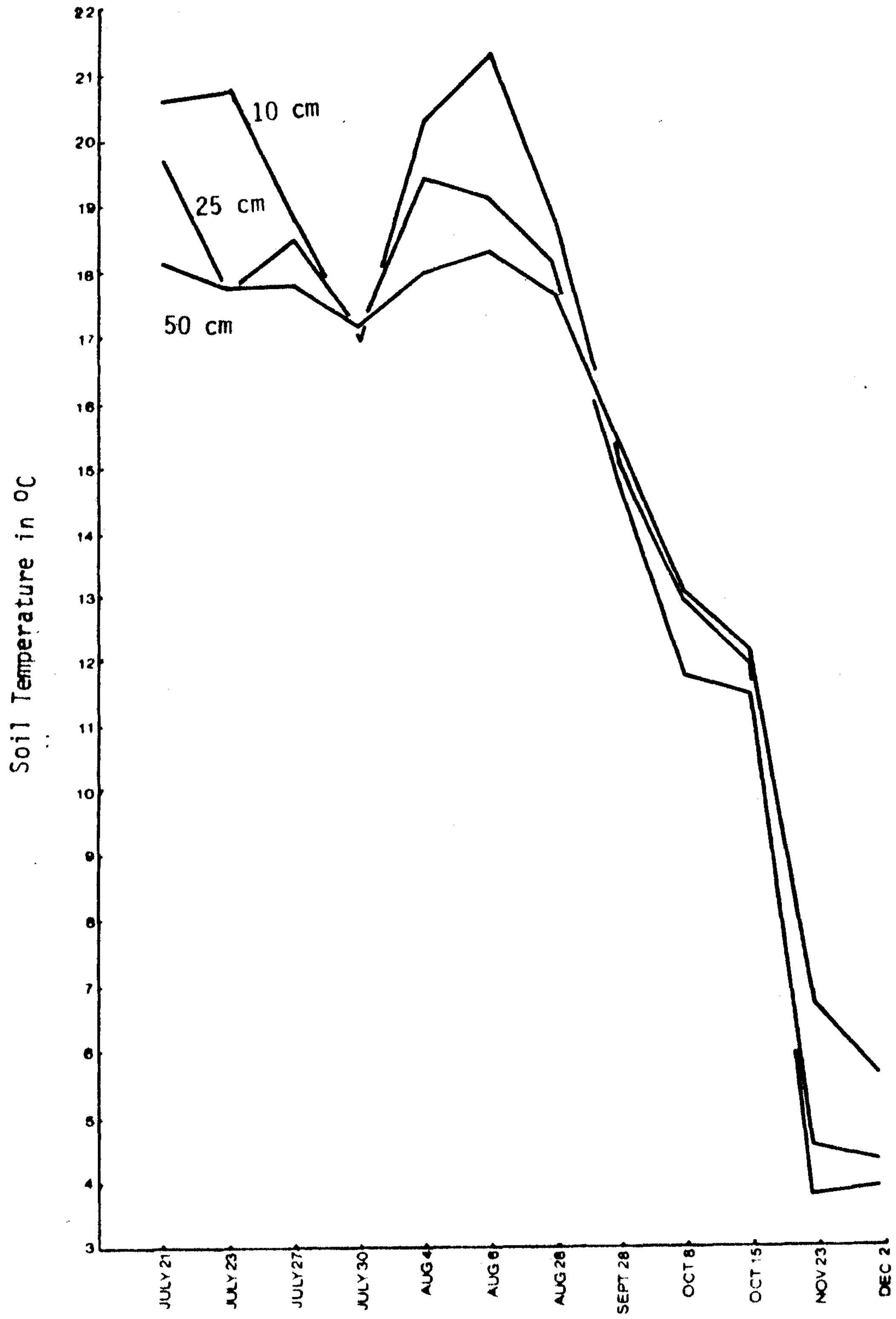

FIGURE 4.3 Mean Temperature for Scrub (S) Sites

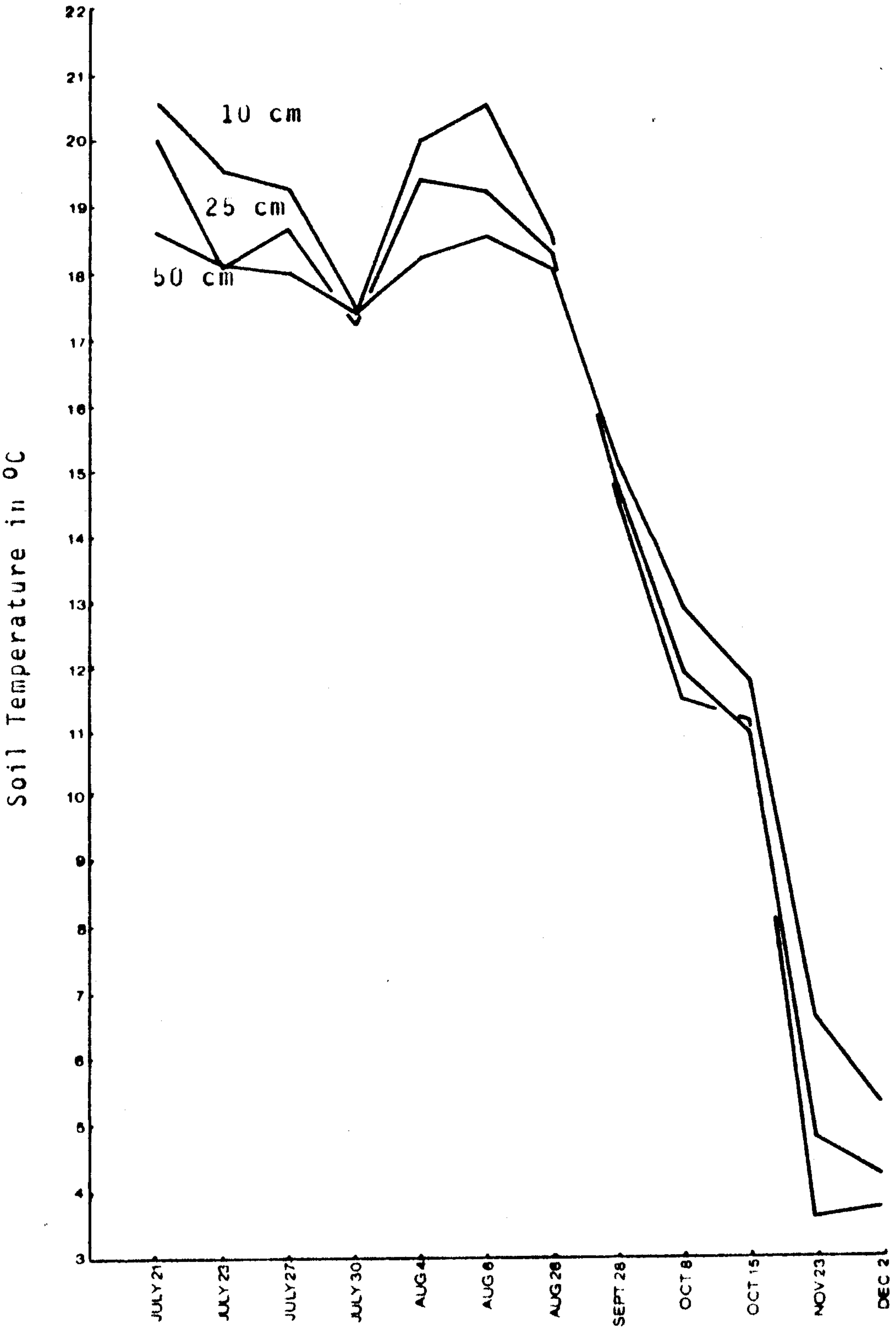

FIGURE 4.4 Mean Temperature for Grass (G) Sites

because the soil receives very little direct solar radiation. The scrub cover has the highest temperatures at 10 cm because the vegetation is sparse at the soil surface and the soil can be heated directly by solar radiation. The grass cover is thick and uncut and the soil surface cannot be heated directly as with the scrub. This insulating ability of vegetation has been recognized by Baver et al (1972) as cited in Toogood (1979).

The increase in soil temperature at any depth is largely the result of the diurnal input of heat by solar radiation. The soil surface, because it is closest to the source of heat, will attain higher temperatures before the soil at some greater depth. During the summer and early fall at Rock Chapel, soil temperatures are greatest at 10 cm depth and, in general, decrease as depth increases. Between August 28 and September 28 this pattern changes for all vegetation types. From September 28 onwards temperatures at 50 cm depth become warm relative to temperatures at 10 and 25 cm. This is the result of the decrease in diurnal heating as winter approaches. The surface of the soil loses heat more quickly than the soil at greater depths thus temperatures increase with depth. At the same time, however, all temperatures are decreasing within the soil profile although not at the same rate.

Over the entire range of dates, seasonal temperature variations under any vegetation type are greatest at 10 cm depth and smallest at 50 cm depth. This corresponds to known soil temperature behaviour as described in section 2.2.5.2. Toogood (1979) also documents that soil temperatures at 20 cm vary much more annually than do temperatures at 100 cm. For any single date the range of temperatures between depths varies from about 0.5°C (scrub or grass, July 30) to about 3.5°C (forest, July 21 or August 4). The reasons for such variations are numerous and some have been mentioned previously (section 2.2.5.2). It is interesting to note that the range of temperatures on July 30 is quite small. For grass and scrub covers the temperatures on July 30 represent the smallest measured range for any date while for the forest cover it is the second smallest. From Appendix II it can be seen that a relatively large precipitation event occurred on July 28 (28.2 mm). It is probable that the closeness of soil temperatures at 10, 25 and 50 cm depths on July 30 was due largely to that precipitation event.

The range of temperatures between the three depths for any single date are greater prior to September 28. As previously mentioned the air temperature (mean daily) is less than the soil temperature by this date and thus the soil acts as a heat source for the atmosphere. The loss of heat from the soil can take place more or less continuously as long as air temperatures are cooler than the soil surface. Uninterrupted cooling of the soil, as opposed to diurnal heating of the soil by incoming radiation (prior to September 28), can account for the smaller ranges between depths from September 28 onwards.

4.6.3 The Behaviour of Soil CO_2 at Rock Chapel

The variation of soil CO_2 concentrations for the three vegetation types are shown in Figure 4.5, 4.6 and 4.7. Each data point is the average of the CO_2 concentration measured at each of two duplicate sites (I and II). Unlike the pattern of soil temperatures, CO_2 does not display any consistent relationships between concentrations meas-

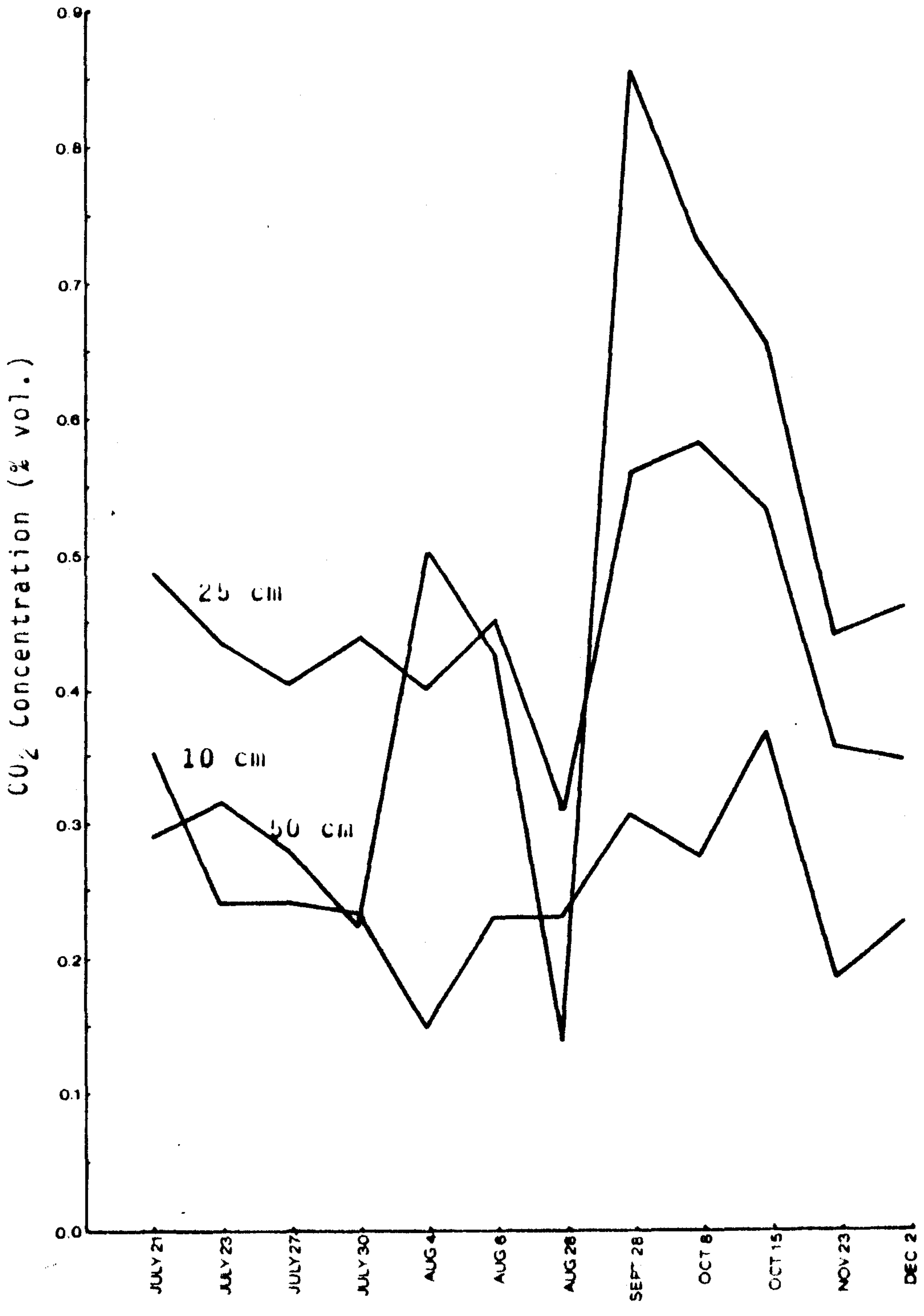

FIGURE 4.5 Mean CO_2 Concentration for Forest (F) Sites

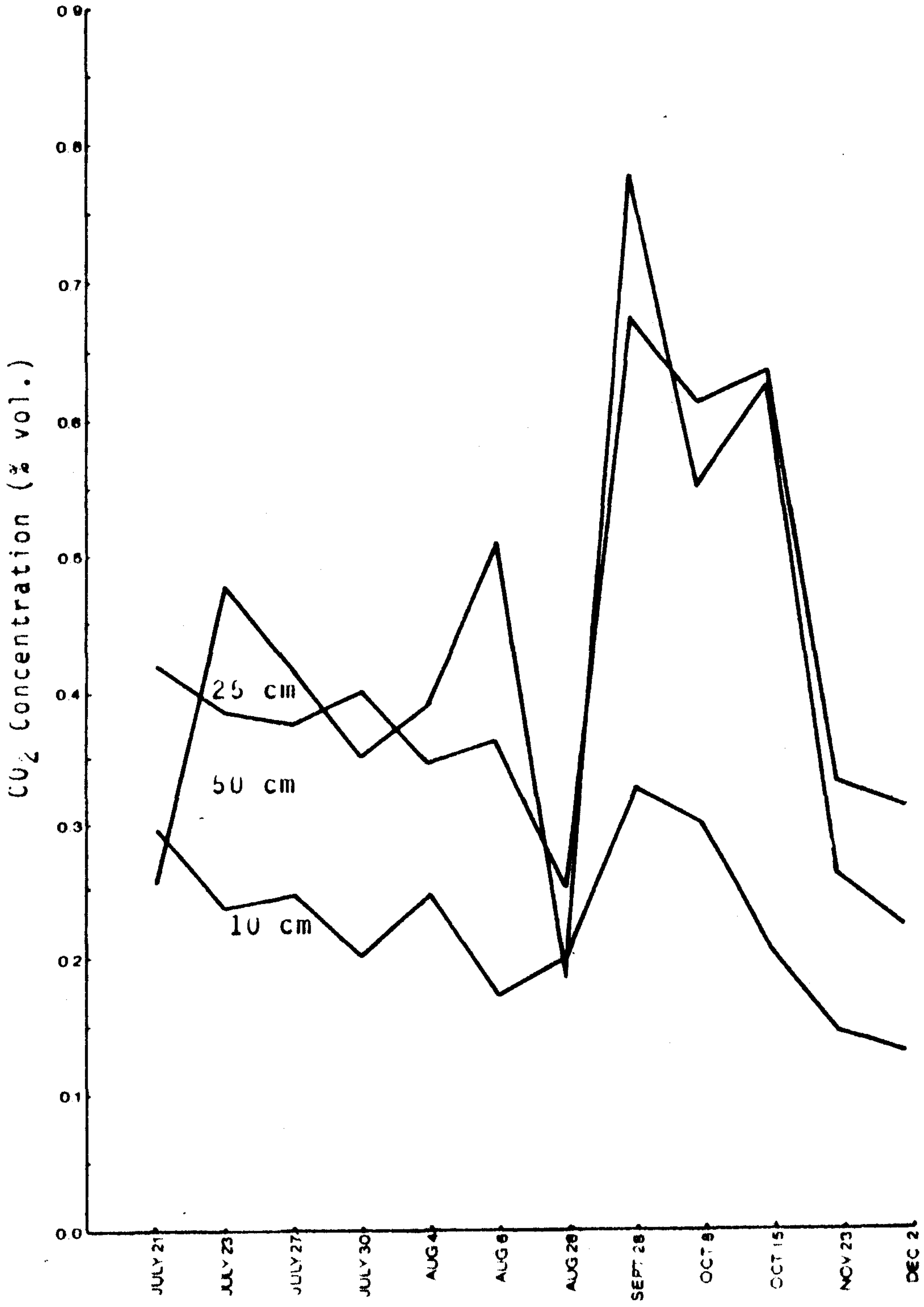

FIGURE 4.6 Mean CO$_2$ Concentration for Scrub (S) Sites

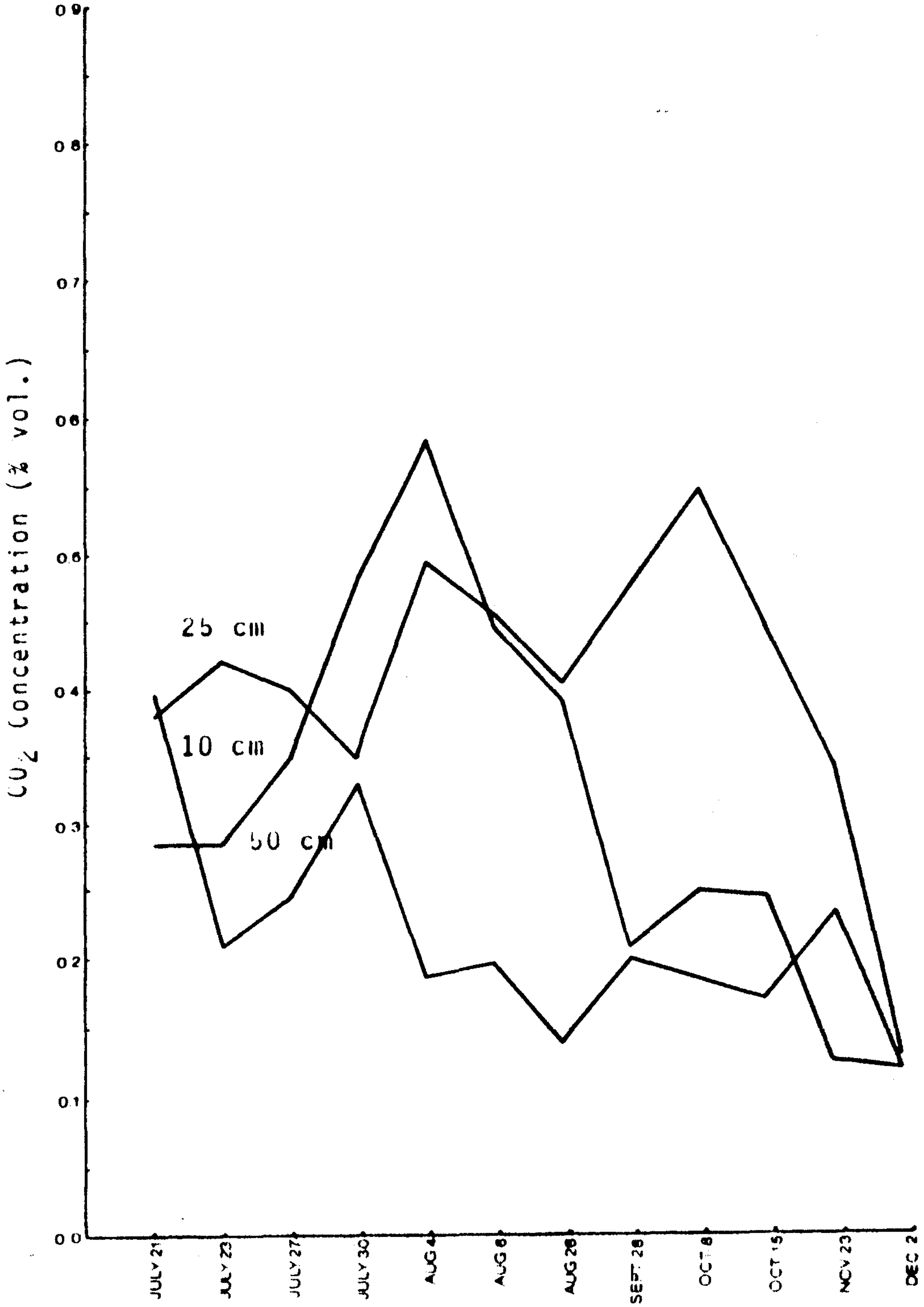

FIGURE 4.7 Mean CO_2 Concentration for Grass (G) Sites

ured at the three depths nor does the overall pattern of variation from date to date for all vegetation types appear similar to the pattern apparent between the soil temperature graphs.

In general, CO_2 concentrations are greatest under the forest cover. Also the average concentration for each depth under the forest cover increases from 10 cm to 25 cm to 50 cm. CO_2 concentrations under the scrub cover are greater than those measured under the grass cover. Unlike the forest, however, the average concentration increases from 10 to 25 cm under scrub and grass, and then decreases slightly at 50 cm.

As mentioned in the previous chapter the 50 cm depth under the forest and scrub covers represents the bedrock-soil interface. Under the grass cover this interface is deeper than 50 cm and is at least 75 cm. The difference between average CO_2 concentrations for 25 and 50 cm depths under grass is greater by an order of magnitude than the same measures under scrub and forest. At 25 cm depth under grass the average concentration is 0.405% CO_2. At 50 cm it is 0.314% CO_2, a difference of greater than 0.09% CO_2. It is suspected that under the grass cover CO_2 concentrations will decrease with further increases in depth.

The grass cover represents a very uniform vegetation cover composed of probably no more than a few species of grass. It would be expected then, that the rooting depth would be at a relatively constant depth in the soil compared to the scrub and forest covers which are composed of a combination of trees, bushes, and grasses. It could be assumed that under the grass cover the rooting depth is somewhere between 25 and 50 cm. Under the forest and scrub covers the entire soil profile (50 cm) likely contains roots. As a result of this, the

CO_2 measured at 25 and 50 cm under forest and scrub varies less than under grass. The greater variety of species which undoubtedly occur in the forest may also help account for the greatest variation in measured concentrations found there. All species do not produce CO_2 at the same rates or under exactly the same conditions. The site that has the greatest variety of species probably experiences the highest concentrations of CO_2 and the greatest range of measured concentrations. The forest cover displays both these attributes to a greater extent than the scrub cover, and the scrub cover to a greater extent than the grass cover.

The maximum combined CO_2 concentration for the three depths occurs on September 28 for both forest and scrub covers. For the grass cover the maximum combined CO_2 concentration is on August 4. None of these maximums represent the beginning of a rapid decrease in measurable CO_2 concentrations corresponding to the end of the growing season. Again it is suspected that the variety of species at the three sites determines, to some extent, the maximum production of CO_2 in the soil. If only one species of vegetation exists at a site the CO_2 in the soil will reflect, somewhat, the productivity of that single species as it is affected by various environmental conditions. If a number of species exist at a site they will react differently to the growth conditions to which they are subjected.

It could be suggested that there is an inverse relationship between soil temperature and soil CO_2. Such a relationship is particularly noticeable at 25 and 50 cm depths. Between July 21 and August 28, when soil temperatures at all depths are greatest, CO_2 concentrations are relatively low. Forest and scrub covers show this behaviour better than the grass cover. As of September 28, when soil temperatures begin to decrease in response to cooler atmospheric temperatures, CO_2 concentrations are greatest under the forest and scrub covers. From October 8 onwards, however, CO_2 and temperature behave as if they are directly related. If an inverse relationship exists between temperature and CO_2, it obviously does not act over the entire range of temperatures measured at Rock Chapel.

4.6.4 The Rock Chapel CO_2 Model

Using analysis of variance testing (ANOVA), described previously in section 4.5, the Rock Chapel data set was manipulated to answer the questions put forward in section 4.6.1. The data set consists of two temperatures and two CO_2 concentrations for each of nine vegetation-depth combinations, on each of twelve different dates. The sampling design is described in more detail in section 3.2.3.

ANOVA testing using BMDP2V (Dixon and Brown, 1977) is extremely comprehensive and can be easily adapted to large data sets. For these reasons BMDP represents a better approach to ANOVA than SPSS (Nie et al, 1975). Used primarily for medical and psychological analyses (see Lindquist, 1956 and Winer, 1971), analysis of variance has also proved useful in geological analyses (see Krumbein and Graybill, 1965 and Davis, 1973).

The Rock Chapel data set is composed of five factors. These are: vegetation, depth, soil temperature, soil CO_2 concentration, and date. The quantitative design used for the ANOVA is similar to an example of a complex design in Dixon and Brown (1977, 568). Vegetation (forest, scrub, grass) and depth (10 cm, 25 cm, 50 cm) are treated as grouping factors, soil temperature as the covariate factor, CO_2 concentration as the dependent factor, and the twelve dates are treated as one level of a repeated measures or trial factor.

The BMDP program P2V, which was used for all ANOVA analyses in this section, assumes that the covariate is linearly related with the dependent factor. In this case soil temperature would be assumed to be linearly related with CO_2. As discussed in section 4.6.3 such an assumption may not be entirely true. The twelve repeated measures in the trial factor, the dates, are also assumed to be independent of each other by the program. For the Rock Chapel data set such an assumption is valid.

The data set was analysed in a number of different ways. The results of the analysis of the full data set are shown in Table 4.10. The upper section of this table includes the analysis of the grouping factors, vegetation and depth, with the covariate and dependent factors, soil temperature and CO_2. The lower section of Table 4.10 includes the analysis of the trial factor and the interaction between the trial and grouping factors. This section also includes soil temperature in the analysis.

From the results of the full analysis it can be seen that three sources of variance are significant as predictors of soil CO_2. These sources are those created by the mean, those created by variations in depth, and those created by changes in CO_2 and temperature over time. Individual analyses of duplicate sites I and II yield slightly differ-

Table 4.10 Results of ANOVA testing of the Rock Chapel Data Set.

Source	Sum Of Squares	D.F.	Mean Square	F	Tail Probability	Beta Estimate
Mean	26.34812	1	26.34812	457.37	.0000*	
V	.16069	2	.08035	1.39	.2967	
D	1.51226	2	.75613	13.13	.0021*	
VD	.09447	4	.02362	.41	.7974	
T	0.00000	0	0.00000	0.00	1.0000	0.00000
Error	.51848	9	.05761	-	-	
R	1.15632	11	.10512	8.06	.0000*	
RV	.62042	22	.02820	2.16	.0054	
RD	.55920	22	.02542	1.95	.0140	
RVD	.67490	44	.01534	1.18	.2517	
T	.00295	1	.00295	.23	.6351	-0.03856
Error	1.27787	98	.01304	-	-	

V=Vegetation D=Depth T=Soil Temperature R=Repeated Measures (dates)

N.B. *'s indicate significance at a 95% level of confidence

ent results. Tables 4.11 and 4.12 show the results of site I and II analyses respectively. For both sites I and II variance as a result of CO_2 and temperature changes over time is significant. At site I, but not site II, the variance introduced by the interaction of the vegetation differences and time is significant. This would seem to indicate differences exist between sites I and II although they are not statistically significant differences. Because sites I and II are less than 10 m from each other in each vegetation type it is difficult to postulate such gross differences between them.

A second series of analyses were performed again using the entire data set and sites I and II individually. This set of analyses differed from the first only in that the relationship between the dependent and the covariate, CO_2 and temperature respectively, was made semi-logarithmic. The results of the ANOVA tests using this transformed data are not particularly different from the original tests except that in the analysis of the entire data set the interaction between the repeated measures factor and vegetation (RV) is significant.

One final analysis did not include the covariate, soil temperature. The results of this test (Table 4.13) indicate that the mean, the depth factor, the repeated measures factor, and the interaction of the repeated measures and vegetation factors, are all significant sources of variance. The ANOVA without temperature produces results comparable to that by logging the relationship between CO_2 and temperature. The prediction of soil CO_2 at Rock Chapel does not necessarily require using soil temperature. Comparable results can be obtained by

Table 4.11 Results of ANOVA testing of Site I Rock Chapel Data.

Source	Sum Of Squares	D.F.	Mean Square	F	Tail Probability	Beta Estimate
Mean	.00122	1	.00122	.09	.7880	
V	.06547	2	.03274	2.31	.2472	
D	.13027	2	.06513	4.59	.1222	
T	.00001	1	.00001	.00	.9795	-.00249
Error	.04254	3	.01418	-	-	
R	.34932	11	.03176	3.71	.0009*	
RV	.47290	22	.02604	3.04	.0009*	
RD	.22890	22	.01040	1.22	.2852	
T	.02397	1	.02397	2.80	.1015	.06222
Error	.36809	43	.00856	-	-	

V=Vegetation D=Depth T=Soil Temperature R=Repeated Measures (dates)

N.B. *'s indicate significance at a 95% level of confidence

Table 4.12 Results of ANOVA testing of Site II Rock Chapel Data.

Source	Sum Of Squares	D.F.	Mean Square	F	Tail Probability	Beta Estimate
Mean	.12708	1	.12708	1.41	.3209	
V	.08414	2	.04207	.47	.6665	
D	.40347	2	.20173	2.23	.2546	
T	.09767	1	.09767	1.08	.3748	-0.17967
Error	.27089	3	.09030	-	-	
R	1.02117	11	.09283	4.56	.0001*	
RV	.36169	22	.01644	.81	.6997	
RD	.54487	22	.02477	1.22	.2839	
T	.05874	1	.05874	2.89	.0965	0.10859
Error	.87492	43	.02035	-	-	

V=Vegetation D=Depth T=Soil Temperature R=Repeated Measures (dates)

N.B. *'s indicate significance at a 95% level of confidence

Table 4.13 Results of ANOVA testing of the Rock Chapel Data Set, CO_2 only - temperature not included

Source	Sum Of Squares	D.F.	Mean Square	F	Tail Probability
Mean	26.34812	1	26.34812	457.37	.0000*
V	.16069	2	.08035	1.39	.2967
D	1.51226	2	.75613	13.13	.0021*
VD	.09447	4	.02537	.41	.7974
Error	.51848	9	.05761	-	-
R	1.21639	11	.11058	8.55	.0000*
RV	.78443	22	.03566	2.76	.0003*
RD	.55813	22	.02537	1.96	.0132
RVD	.73380	44	.01668	1.29	.1503
Error	1.28083	99	.01294	-	-

V=Vegetation D=Depth T=Soil Temperature R=Repeated Measures (dates)

N.B. *'s indicate significance at a 95% level of confidence

either logging temperature with CO_2 or ignoring temperature altogether. Obviously it is a simpler matter to ignore soil temperature than to assume a log-linear relationship between temperature and CO_2. However, a different transformation of the temperature-CO_2 relationship may produce better results than those given here.

Finally the effect of vegetation cover on CO_2 concentrations is not a source of significant variance except when analysed in conjunction with the repeated measures factor. The effect of vegetation cover on CO_2 at any one point in time is insignificant. Over a period of time in which different, seasonal conditions can be experienced, vegetation differences produce significant variations in CO_2.

The model derived for the prediction of soil CO_2 at Rock Chapel has the general form:

$$E(CO_2)_i = \mu + D_i + \varepsilon_i$$

where $E(CO_2)_i$ = the predicted value of CO_2 at depth i (% vol.)

μ = the overall mean of CO_2 measurements made at Rock Chapel

D_i = the difference between the overall mean concentration and the concentration at depth i

and ε_i = the variance of CO_2 at depth i assuming a normal distribution and a mean of zero.

Three equations in this form result from ANOVA testing of Rock Chapel data. Each equation corresponds to one depth (10, 25, or 50 cm). The equations are:

$$E(CO_2)_{10} = .349 + (-.117) \pm .007$$

$$E(CO_2)_{25} = .349 + (\ .075) \pm .021$$

$$E(CO_2)_{50} = .349 + (\ .043) \quad .048.$$

This model of CO_2 is based on the assumption that the range of CO_2 measurements made in the field will be normally distributed. It also takes into account variations in CO_2 as a result of seasonal (July-December) effects.

The interaction of CO_2 variations due to vegetation differences and the repeated measures factor also yields an equation for predicting CO_2. Since there are twelve dates and three vegetation types in the data set, there are 36 combinations of date and vegetation to be accounted for. In view of this the three depth equations are more useful, although more general, for predictive purposes. The repeated measures factor would be more useful if measurements were made at specific intervals over the period of one year. The repeated measures could then be analysed as seasonal effects thus reducing the number of equations required when dealing with single dates.

CHAPTER 5

SUMMARY, CONCLUSIONS AND SUGGESTIONS FOR FUTURE RESEARCH

5.1 Summary

The research described in the preceding four chapters was performed with three objectives in mind. The first objective, which was to summarize a broad range of soil CO_2 research, was the most straightforward objective and the easiest one to meet. Most soil CO_2 data do not come from karst research but from the fields of soil science, ecology and forestry. As such the techniques and requirements of the researchers measuring soil CO_2 vary considerably. Techniques as well as the variability and availability of CO_2 are described along with some general conclusions drawn from the literature.

The second objective involved describing the Dräger gas pump and vacutainer-IRGA methods of CO_2 measurement. The various tests performed on each of these methods probably presents the most extensive analysis of their viability as tools for karst research yet published.

The third objective, the development and description of a model which predicts CO_2, was the most difficult objective to meet. The derivation of the model is based upon a data set which includes coincident soil temperature and CO_2 measurements taken at nine different vegetation-depth combinations over a period of six months. Analysis of variance testing using BMDP was performed on the data set. The results of the ANOVA tests were used to determine the components of the model.

5.2 Conclusions

Only general conclusions regarding the second and third objectives will be mentioned here. Specific results will not be reiterated either.

Both the Dräger and the vacutainer-IRGA methods are viable techniques for measuring soil CO_2. Understandably each method has its own particular advantages and disadvantages. The vacutainer-IRGA method is more complex than the Dräger method, probably allowing more variability in its determinations as a result of operator errors. On the other hand the Dräger method may be more susceptible to imprecise CO_2 measurements as a result of the volume of soil air it requires. The vacutainer-IRGA field sampling device can be much more flexible and accurate in terms of repetitive and duplicate sampling schemes than the Miller-Dräger apparatus. For remote locations, however, where logistics cannot support a gas chromatograph or infrared gas analyser, the Dräger method will undoubtedly prove more suitable. Furthermore, for very short term projects the Dräger may become an economic choice unless access to chromatographs or gas analysers is obtainable. The accuracy of each method is comparable.

The Rock Chapel CO_2 model, although appearing simple, has taken into account a number of variables, several of which were found to introduce insignificant variance into CO_2 measurements. The general model, then, is based on CO_2 variations resulting from differences in depth. The three depths at which measurements were taken were only 40 cm apart. This indicates that a strict control of depth should be maintained during repetitive measurements. Although vegetation differences seem large, for example forest vs. grass, no statistical differentiation between vegetation covers could be made.

5.3 Suggestions for Future Research

As intimated in section 2.3, the link between the present understanding of CO_2 in the unsaturated zone of the soil and the present understanding of carbonate water chemistry could be strengthened. This approach to karst from the viewpoint of determining what is taking place at or near the surface of the earth in order to better understand what is taking place at depth in the soil or bedrock, is not new but should, perhaps, be re-evaluated. However, unless soil CO_2 data is gathered in a reasonable, consistent manner by researchers, such an approach will be worthless. Within the literature several reports exist (eg. Miller, 1981; Gunn and Trudgill, 1982) where the author(s) have not measured CO_2 at a specific depth in the soil. Unless repetitive measures are made at consistent depths in the soil, that is corresponding to some regularity either in the sampling design or in the physical characteristics of the soil, and at regular time intervals or intervals corresponding to some occurrence of phenomena inducing changes to soil CO_2 concentrations, conclusions drawn from the data could be spurious. As seen from the ANOVA results in the previous chapter, CO_2 variations between depths of 10, 25, and 50 cm were always found to be a significant source of variance when the full data set was analysed.

APPENDIX I

Tree Species found at Rock Chapel Sanctuary

Shagbark Hickory
Basswood
Hawthorn
Chinquapin Oak
Hop Hornbeam (Ironwood)
Sugar Maple
Allegheny Serviceberry
White Birch
White Oak
Red Oak
Eastern Red Cedar (Red Juniper)
Witch Hazel
Black Cherry
White elm
Blue beech
Pin Cherry
Eastern White Pine
Wild Crab Apple (Sweet Crab Apple)
Black Walnut
Volunteer Pear

SOURCE: field observations

APPENDIX II

1981 Mean Daily Temperature Hamilton Airport

(°C)

	July	Aug.	Sept.	Oct.	Nov.	Dec.
1	18.5	21.5	23.2	10.6	10.4	2.2
2	20.3	22.2	22.8	5.6	10.4	4.1
3	21.2	22.4	20.3	5.9	7.8	1.1
4	23.3	22.2	20.9	6.2	9.0	1.0
5	21.5	22.3	19.4	13.0	8.0	-0.5
6	23.0	19.5	19.4	13.9	5.6	-1.7
7	24.2	21.2	20.2	7.5	2.9	2.7
8	25.6	19.8	16.4	7.3	6.4	-1.5
9	25.1	20.7	13.1	6.4	1.4	-5.7
10	20.8	21.5	18.0	6.8	-0.6	-6.5
11	22.5	19.4	17.3	7.5	3.2	-2.5
12	23.1	19.4	19.3	7.2	-1.2	-4.5
13	24.5	21.9	19.5	7.7	3.5	-1.9
14	18.9	22.4	19.8	9.8	4.7	-1.2
15	19.7	18.7	14.7	11.0	7.6	-0.2
16	20.6	16.5	13.5	7.2	8.0	-2.5
17	20.8	16.4	11.8	6.0	7.2	-5.7
18	22.5	15.9	11.3	8.8	6.1	-8.2
19	24.5	17.2	11.1	1.9	3.8	-9.4
20	21.4	18.8	9.8	8.9	3.8	-9.4
21	17.8	20.0	8.6	5.4	0.9	-3.5
22	15.9	20.9	9.3	2.4	-0.9	0.3
23	15.7	19.6	8.8	4.3	-1.1	0.2
24	18.2	17.7	10.3	1.0	-1.8	-2.4
25	20.9	17.5	13.0	4.5	-2.2	-4.3
26	20.2	19.4	17.0	6.8	4.3	-2.7
27	18.7	18.3	16.9	8.8	7.0	-1.4
28	15.3	18.2	7.8	7.4	2.5	-1.8
29	17.2	21.7	7.4	5.0	0.3	-4.2
30	18.9	20.8	6.2	6.6	0.5	-6.4
31	20.2	21.6	-	7.5	-	-1.5

APPENDIX II (con't.)

1981 Precipitation Hamilton Airport
(mm, unless otherwise specified)

	July	Aug.	Sept.	Oct.	Nov.	Dec.
1	1.4		5.6	12.1		7.4/T(s)
2	0.4	T	21.4	0.2		T
3		10.6	17.8			
4	0.2	0.2	11.8	0.2		T(s)
5	2.8		27.3		T	T(s)
6				12.3	2.8/0.4 cm	
7		T	T	T		
8		90.8	7.9			2.2/4.2 cm
9	3.8	T	T			T(s)
10		1.6				T(s)
11		23.4				T(s)
12		T				
13	T	52.8				
14			0.2	0.2		T(s)
15		10.6		0.2		T(s)
16			0.8		7.3	0.4 cm
17			13.5		1.9	3.2 cm
18	34.0			15.0	T	
19				0.6/0.6 cm	1.6	0.6 cm
20					23.9	T(s)
21			23.6	7.5	T/1.2 cm	T/4.8 cm
22			2.4	11.6	T(s)	0.8/4.0 cm
23				1.6/0.6 cm	T(s)	14.2/0.2 cm
24		1.0				
25			2.6			
26	0.2		1.6	6.2	6.5	0.4 cm
27		1.2	0.4	18.0	T	3.4 cm
28	28.2	3.4			T(s)	5.4 cm
29	2.8	1.4			0.2 cm	1.2 cm
30		31.9	2.2			
31			-		-	5.8/0.2 cm

T = trace of rain
T(s) = trace of snow

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