A STUDY OF THE HYDROCHEMISTRY OF A LIMESTONE AREA: BUCHAN, EAST GIPPSLAND.

by

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ABSTRACT

This thesis reports the results obtained, and conclusions made regarding research into the hydrochemisty of a small impounded karst area in southeastern Australia.

Water samples were collected from a variety of sites over a period of approximately six years and include samples that are representative of baseflow (drought conditions) and flood (high flow conditions) the two extremes of the flow regime.

Four distinct water types were found to be associated with the karst spring and cave water sites sampled. In terms of physical, chemical and computed parameter values these have been classed as TYPE 1 water (median parameter values similar to those noted for the surface stream sites sampled with catchments of non-carbonate material); TYPE 2 water (catchment predominantly of limestone); TYPE 3 water (catchment predominantly of dolomite); TYPE 4 water (high median chemical concentrations).

Spatial variation within the study area is considerable and intrinsic factors such as catchment lithology, the residence time of recharge, aspect and vegetation cover are the major natural controls in determining physical and chemical characteristics.

Four flow types can be identified in the karst spring and cave water sites and range from predominantly conduit flow through to diffuse flow systems. Flow types can be distinguished by using the co-efficient of variation of total hardness, the co-efficient of variation of water temperature and the median SI_{cal} value obtained for each site.

A value for the co-efficient of variation of total hardness of around 25% (notably higher that used to differentiate between conduit and diffuse flow systems in the northern hemisphere) is used to differentiate between mixed conduit/diffuse and predominantly diffuse flow systems. The higher value found in this study is a reflection of the inherent hydrological variability associated with many systems in Australia, in particular those in southeastern Australia.

Karst spring sites where the largest tufa deposits occur are associated with diffuse or predominantly diffuse flow systems that record a median $SI_{cal} > 0.50$. Both inorganic and organic processes control tufa deposition; inorganic processes dominate where strongly turbulent flow occurs and organic processes dominate where flow is retarded and aquatic vegetation thrives.

DECLARATION

This thesis is the result of research carried out by the author over a period of eight years of part-time study. This thesis contains no material which has been accepted for the award of any other degree or diploma in any university or institution and to the best of the author's knowledge, contains no material previously written or published by another person except where due reference is made in the text. The length of this thesis is less than 100,000 words exclusive of tables, figures, bibliography and appendices.

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CHAPTER ONE

PREAMBLE

INTRODUCTION

The alteration and solution of rock material by chemical weathering processes imparts particular chemical characteristics to natural ground and surface waters. Chemical weathering is largely accomplished by rain water acting as a carrier of dissolved carbon dioxide, together with various acids and organic products derived from the soil. The variety of dissolved constituents found in such waters can allow one to make certain deductions about their chemical origin. In many parts of the world the results obtained from the chemical analyses of dissolved constituents in surface and ground waters, sampled either on a local or regional basis, have been used to evaluate and identify lithologic effects and source areas (Meisler and Becher, 1967; Long and Saleem, 1974; Reinson, 1976; Trainer and Heath, 1976; Rosenthal and Mandel, 1985; Ramamurthy et al, 1985; Sen and Al-Dakheel, 1986; Rosenthal, 1987; 1988).

Dissolved constituents (usually designated as that which passes through a filter of a particular pore size) can enter into solution through a variety of chemical reactions depending primarily upon which mineral or minerals are involved and other physico-chemical characteristics such as temperature, gas pressures, rate of reaction, etc.. The more variables that are involved in a particular system the harder it is to assign the chemical species found to particular chemical reactions. The dissolution of minerals such as halite (NaCl) and gypsum ($CaSO_4.2H_2O$) proceed very rapidly under most atmospheric conditions that occur at, or near the earth's surface, whereas for the dissolution of calcite ($CaCO_3$) or some of the silicate minerals quite a number of variables, even at constant temperature and pressure, are involved. For instance, Garrels and Christ (1965) found that there were at the most, seven variables involved (at constant temperature and pressure) when they considered the solubility of pure calcite under five theoretically different geological environments. It is the dissolution of calcite and dolomite, the two major components of limestone terrains, and the release of chemical species from these two minerals to natural ground and surface waters that is the main concern of this thesis.

CARBONATE SOLUTION

In their most generalised form the solution of calcite and dolomite may be summarised by the following reactions,

$$\underset{\text{(calcite)}}{CaCO_3} + \underset{\text{(water)}}{H_2O} + \underset{\text{(carbon dioxide)}}{CO_2} <=> \underset{\text{(dissolved calcite)}}{2HCO_3^- + Ca^{2+}} \quad (1.1)$$

$$\underset{\text{(dolomite)}}{CaMg(CO_3)_2} + \underset{\text{(water)}}{2H_2O} + \underset{\text{(carbon dioxide)}}{2CO_2} <=> \underset{\text{(dissolved dolomite)}}{4HCO_3^- + Mg^{2+} + Ca^{2+}} \quad (1.2)$$

Thus, by the chemical analysis of waters that drain from a carbonate terrain, i.e. by determining how much Ca^{2+}, Mg^{2+} and HCO_3^- are in solution (assuming no outside input) one can determine solutional processes and rates operating in a particular carbonate region. It must be remembered that the two reactions above are greatly oversimplified and that the actual processes of dissolution are quite complicated and comprise a number of reversible and mutually interdependent reactions each with its own rate and equilibrium constant. These equilibrium and rate effects are discussed in more detail in this Chapter under the sections headed Equilibria Mechanisms and Chemical Kinetics and Transport Mechanisms respectively. The concentration of ions in a particular water derived from the dissolution of limestone or dolomite depends primarily on two sets of factors :- i) equilibrium factors which determine the mineral solubility, and, ii) kinetic-dynamic factors which determine the extent to which a water has obtained chemical equilibrium, and according to Ollier (1982, p.40), "it is of the utmost importance in understanding limestone solution to distinguish between equilibrium and kinetic factors".

EQUILIBRIA MECHANISMS

This section provides a brief overview of equilibrium factors and for detailed explanations and discussions the reader is referred to Garrels and Christ (1965), Roques (1969), Bögli (1980), White (1984), Trudgill (1985) and Dreybrodt (1988).

Laboratory studies have shown that the solubility of calcite in pure water is about 14.0mg/l at 25°C (Picknett, 1973) and slightly lower for dolomite, yet greater concentrations of calcium and magnesium ions have been found in waters draining from carbonate terrains than that predicted for pure water, indicating a substantial increase in solubility. This can be explained by absorption by water of carbon dioxide from the atmosphere, and more importantly, from that derived by biological processes in the soil and the subsequent formation of carbonic acid (Smith and Atkinson, 1976; Palmer, 1984; Jennings, 1985; Ritter, 1986). This "CO_2 effect" appears to far outweigh any differences noted between solubility values obtained in the laboratory and those in the field. In the following discussion the term limestone will be used to denote both limestone and dolomite unless otherwise stipulated.

H_2O – $CaCO_3$ SYSTEM

In a closed pure water – calcite system, i.e. with no transport of ions or water into or out of the system, $CaCO_3$ readily dissociates at the solid – liquid interface with diffusion of Ca^{2+} and CO_3^{2-} ions away from the crystal lattice structure into the bulk of the solution (Figure 1.1). Dissociation of solid $CaCO_3$ can be depicted by the following reaction,

$$CaCO_{3(solid)} \quad <=> \quad Ca^{2+} \quad + \quad CO_3^{2-} \qquad (1.3)$$

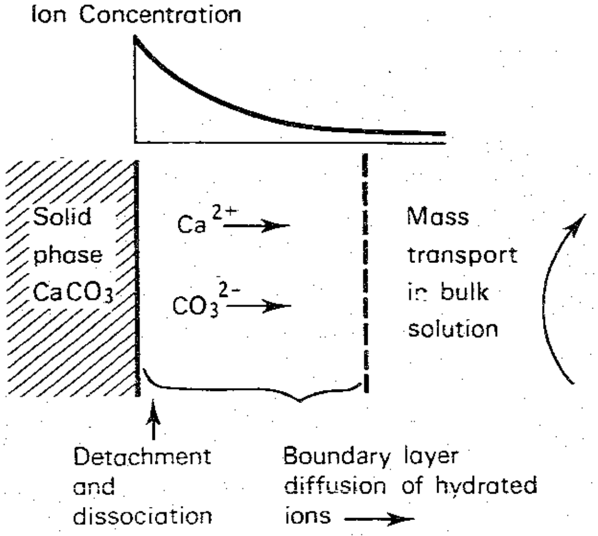

Figure 1.1. Simple dissolution of calcium carbonate in pure water; dissociation and diffusion down the concentration gradient are the main processes involved; mass transport in the bulk solution may act to maintain a steep concentration gradient. (After Trudgill, 1985).

Initial movement of ions away from the crystal lattice is rapid and a steep diffusion gradient is established from the solid to the liquid. Solute concentration will increase over time with a decreasing gradient until saturation concentration is achieved (Figure 1.2). Some of the carbonate ions from reaction (1.3) combine with hydrogen ions, which are always present in water, to form bicarbonate ions,

$$CO_3^{2-} \quad + \quad H^+ \quad <=> \quad HCO_3^- \qquad (1.4)$$

Some of the bicarbonate ions also combine with hydrogen ions to form carbonic acid,

$$HCO_3^- + H^+ \Leftrightarrow H_2CO_3 \qquad (1.5)$$

After a time, t, equilibrium is established in which the forward and reverse reaction rates of the above reactions are equal (Figure 1.3a), i.e. dissolution is equal to precipitation (Figure 1.3b) and the solution is saturated with calcium carbonate such that,

$$K_{cal} = (Ca^{2+})_{eq}(CO_3^{2-})_{eq} \qquad (1.6)$$

where K_{cal} is the solubility product of calcite (3.8×10^{-9} at 20°C; Picknett, 1973)) and the round brackets denote activities (molar concentrations multiplied by the activity co-efficient of the particular ion).

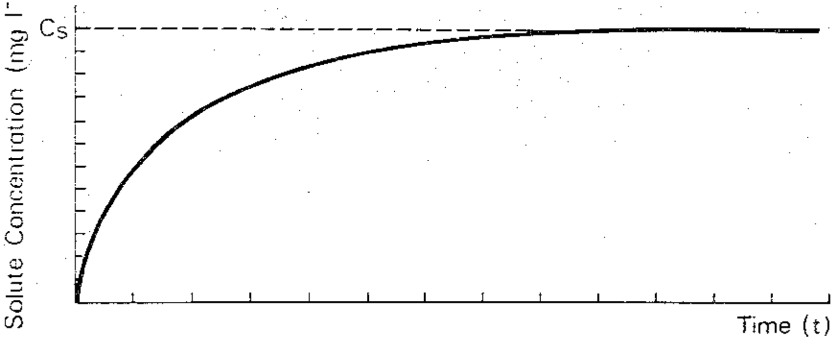

Figure 1.2. Increase of solute concentration over time in a closed system. The concentration C_s is the saturation concentration. The units will be defined for any one solute under given conditions. (After Trudgill, 1985).

It can be seen then that the addition of any hydrogen ions (from an acid) to the above system, will displace the equilibrium established in reactions (1.4) and (1.5) in a forward direction and reduce $[CO_3^{2-}]$ and $[HCO_3^-]$. (Note square brackets indicate molar concentration).

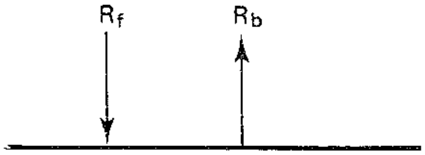

Figure 1.3a. At equilibrium the forward reaction, Rf, is equal to the back reaction, R_b. (After Trudgill, 1985).

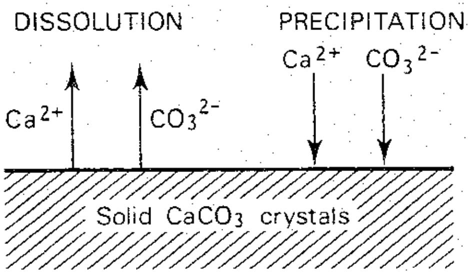

Figure 1.3b. Calcium carbonate in pure water in a closed system at equilibrium. (After Trudgill, 1985).

The ionic activity product, $(Ca^{2+}).(CO_3^{2-})$, of reaction (1.3) no longer corresponds to the solubility product K_{cal}, i.e. K_{cal} is disturbed by an imbalance in the solutions equilibrium with solid $CaCO_3$ by a depletion in $[CO_3^{2-}]$, so more $CaCO_3$ dissolves to re-establish equilibrium, i.e. K_{cal} = constant (which is dependent on temperature and the partial pressure of carbon dioxide), whereby $[Ca^{2+}]$ increasingly predominates over $[CO_3^{2-}]$ due to reaction (1.4).

CO_2 - H_2O - $CaCO_3$ SYSTEM

As previously noted, the adsorption of CO_2 by water and the formation of H_2CO_3, a weak acid, is probably the most important process in the dissolution of limestones. In the system CO_2 - H_2O - $CaCO_3$, essentially the following takes place (after Bögli, 1980), with an overview given in Figure 1.4:

(a) Prior to any dissolution of $CaCO_3$, CO_2 diffuses into water,

$$CO_{2(gas)} + H_2O <=> CO_{2(aq)} + H_2O \qquad (1.7)$$

(b) $CO_{2(aq)}$ reacts with water to form carbonic acid,

$$CO_{2(aq)} + H_2O <=> H_2CO_3 \qquad (1.8)$$

(c) As an acid H_2CO_3 rapidly dissociates, and this yields a source of acidity in water,

$$H_2CO_3 <=> H^+ + HCO_3^- \qquad (1.9)$$

The bicarbonate ion also dissociates,

$$HCO_3^- <=> H^+ + CO_3^{2-} \qquad (1.10)$$

but at a pH < 8.3, which is generally the case for most natural waters, CO_3^{2-} can be neglected because of its small proportion. Dissociation of H_2CO_3 into HCO_3^- and CO_3^{2-} is controlled by pH as a master variable (this is

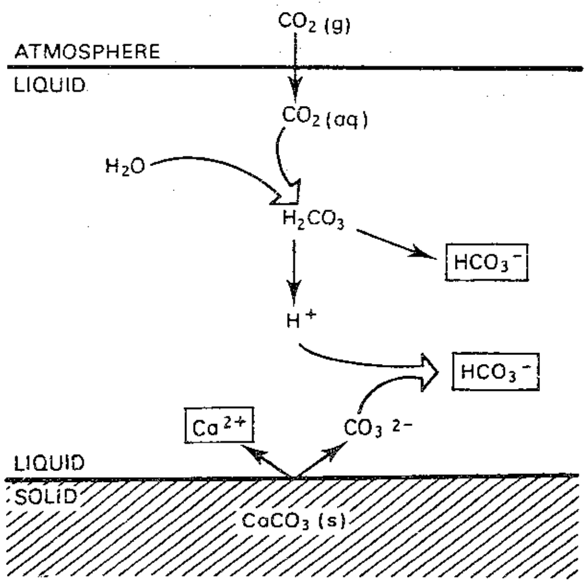

Figure 1.4. Reactants and products during calcium carbonate dissolution in the presence of carbon dioxide: $CaCO_3 + CO_2 + H_2O -> Ca^{2+} + 2HCO_3^-$ □ = products in solution. (After Trudgill, 1985).

examined in more detail in the discussion on equilibrium constants), and

(d) Solid $CaCO_3$ dissociates when in contact with water,

$$CaCO_{3(solid)} \langle = \rangle Ca^{2+} + CO_3^{2-} \qquad (1.11)$$

As in the H_2O – $CaCO_3$ system the ionic activity product is disturbed by association of H^+ ions from (1.9) with CO_3^{2-} ions from (1.11) and renewed dissociation of H_2CO_3 takes place. But in this system another variable, carbon dioxide, must be taken into account. The equilibrium established between $CO_{2(aq)}$ and H_2O (1.8) is disturbed by the lower $[H^+]$, and new CO_2 from the atmosphere diffuses into the solution to restore equilibrium, hence all steps are re-activated until new equilibrium conditions are established. It must be remembered that these reactions are all dynamic and in the natural environment boundary conditions will be constantly changing and hence equilibria will be established, disturbed, re-established, etc. It can be seen then that to a large extent $[CO_{2(aq)}]$ controls the solubility of limestones.

EQUILIBRIUM CONSTANTS

For the general reaction,

$$aA + bB \langle = \rangle cC + dD$$

an equilibrium constant, K, can be used to describe chemical equilibria, i.e.

$$K = \{\gamma_c[C].\gamma_d[D]\}/\{\gamma_a[A].\gamma_b[B]\} \quad (1.12)$$

where $\gamma_n[N] = (N)$, and γ_n is the individual ion activity coefficient of the ion N and K has a fixed value for any given temperature. Individual ion activity coefficients can be calculated by using the Debye - Hückel equation where,

$$\log\gamma_n = \{-Az_n^2.\sqrt{I}\}/\{1 + Ba_n\sqrt{I}\} \quad (1.13)$$

$A = .4883 + (8.074 \times 10^{-4})T$, $B = .3241 + (1.6 \times 10^{-4})T$ ($T = T^\circ C$), z_n = charge of the particular ion, a_n = hydrated radius of the particular ion and I = ionic strength of the solution. Ionic strength of the solution is related to charge and concentration of the ions in solution by,

$$I = 1/2\{\Sigma_i z_i^2.c_i\} \quad (1.14)$$

where z_i is the charge of the i-th species in solution and c_i is the concentration of the i-th ion in mol l^{-1}.

For the pure H_2O - $CaCO_3$ - CO_2 system the ionic and molecular species most commonly accepted as being present are, H^+, OH^-, Ca^{2+}, CO_3^{2-}, HCO_3^-, H_2CO_3, $CaCO_3^o$, CO_2^o and $CaHCO_3^+$ (Picknett, 1973; Picknett et al, 1976). The index ^{o} identifies the molecules as being in solution instead of in a solid or a gaseous phase. The concentration of the ion-pair $CaHCO_3^+$ and also that of $CaCO_3^o$ and the incorporation of these molecules into aqueous models describing calcite dissolution is disputed. Plummer and Busenberg (1982) in their study of the solubilities of calcite, aragonite and vaterite between 0° and 90°C considered the concentrations of these two molecules to be quite important, but others such as Langmuir (1971a), Wigley (1973), Dreybrodt (1981) and Dreybrodt (1988) neglect $[CaHCO_3^+]$ and $[CaCO_3^o]$ on the assumption that their relative concentrations are negligible within the temperature and pH ranges found for the majority of natural karst waters.

For the chemical reactions most commonly used to describe calcite dissolution,

$$CO_{2(gas)} + H_2O <=> CO_{2(aq)} + H_2O <=> H_2CO_3 \qquad (1.15)$$

$$H_2CO_3 <=> HCO_3^- + H^+ \qquad (1.16)$$

$$HCO_3^- <=> CO_3^{2-} + H^+ \qquad (1.17)$$

$$CaCO_{3(solid)} <=> Ca^{2+} + CO_3^{2-} \qquad (1.18)$$

$$H_2O <=> H^+ + OH^- \qquad (1.19)$$

when equilibrium is reached the concentration of each ion is invariant and the concentrations of the ions are related to one another by equations involving equilibrium constants, i.e.

$$K_{CO2} = (H_2CO_3)/PCO_2 \qquad (1.20)$$

$$K_1 = \{(HCO_3)(H^+)\}/(H_2CO_3) \qquad (1.21)$$

$$K_2 = \{(CO_3^{2-})(H^+)\}/(HCO_3^-) \qquad (1.22)$$

$$K_{cal} = (Ca^{2+})(CO_3^{2-}) \qquad (1.23)$$

$$K_w = (H^+)(OH^-) \qquad (1.24)$$

For dolomite,

$$K_{dol} = (Ca^{2+})(Mg^{2+})(CO_3^{2-})^2 \qquad (1.25)$$

Numerical values for these equilibrium constants at various temperatures are listed in Table 1.1.

TABLE 1.1. EQUILIBRIUM CONSTANTS FOR CARBONATE REACTIONS. (${}_pK = -\log K$)

T(°C)	${}_pK_w$	${}_pK_{CO2}$	${}_pK_1$	${}_pK_2$	${}_pK_{cal}$	${}_pK_{dol}$
0.0	14.94	1.11	6.58	10.62	8.22	16.56
5.0	14.73	1.19	6.52	10.55	8.24	16.63
10.0	14.53	1.27	6.46	10.49	8.26	16.71
15.0	14.35	1.34	6.42	10.43	8.28	16.79
20.0	14.17	1.41	6.38	10.38	8.31	16.89
25.0	14.00	1.47	6.35	10.33	8.34	17.00
30.0	13.83	1.52	6.33	10.29	8.37	17.12
35.0	13.68	1.58	6.31	10.25	8.41	17.25
40.0	13.53	1.68	6.30	10.22	8.58	17.39

(Source: White, 1988).

As noted previously pH is a master variable and by using the equilibrium constants, K_1 and K_2 (equations (1.21) and (1.22)), the ionic fractions of individual species in the $H_2O - CO_{2(aq)}$ system as a function of pH can be calculated (Figure 1.5).

For pH < 4 virtually no HCO_3^- and CO_3^{2-} ions are present in solution only $H_2CO_3^*$ exists ($[H_2CO_3^*] = [CO_{2(aq)}] + [H_2CO_3]$). As pH increases H_2CO_3 dissociates forming HCO_3^- until at pH values close to 6.4 both species are present in comparable molar fractions. For pH < 8.3 virtually no CO_3^{2-} is present. For pH > 8.3 HCO_3^- starts to dissociate until at pH 10.33 molar fractions of HCO_3^- and CO_3^{2-} are comparable, for pH > 12 only CO_3^{2-} ions are present.

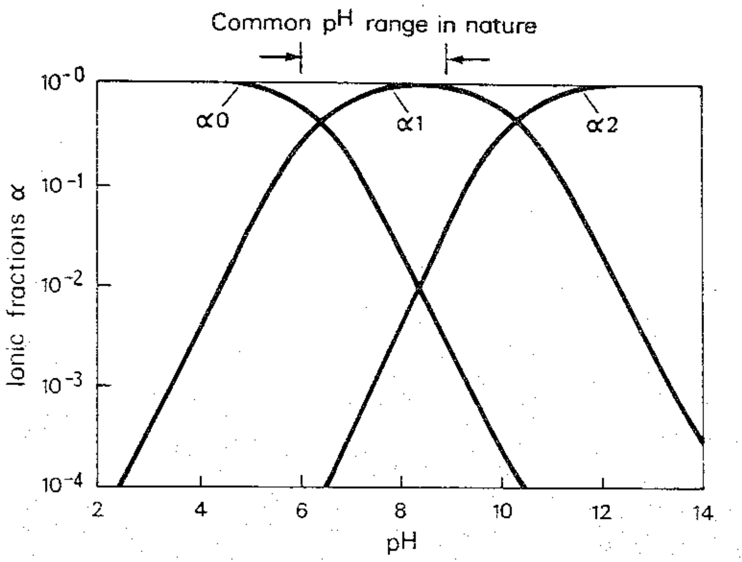

Figure 1.5. Ionic fractions of $H_2CO_3^*$ as α_0, HCO_3^- as α_1 and CO_3^{2-} as α_2 as a function of pH in the solution. Note that the scale of the ordinate is logarithmetic. $\alpha_0 = [H_2CO_3^*]/C_T$, $\alpha_1 = [HCO_3^-]/C_T$, $\alpha_2 = CO_3^{2-}]/C_T$, and $C_T = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}]$. ($C_T$ = total amount of carbon in solution in a CO_2 - H_2O system). (After Dreybrodt, 1988).

CARBON DIOXIDE AND ITS ROLE IN CARBONATE DISSOLUTION

For the CO_2 - H_2O - $CaCO_3$ system two possible situations can be looked at, i) the system is open to the "atmosphere", i.e. the system is open to a fixed partial pressure of carbon dioxide and gaseous exchange is possible, i.e. as $[CO_{2(aq)}]$ decreases due to calcite dissolution, there is an "open reservoir" of $CO_{2(gas)}$ to replenish the system until equilibrium is eventually achieved. Using the equilibrium constants and chemical reactions given in the previous section it is possible to plot a graph relating carbon dioxide content of the gas phase to the total amount of $CaCO_3$ that an equilibrium solution can dissolve (Figure 1.6), and, ii) the system is closed, in this system water comes to an initial equilibrium with [$CO_{2(gas)}$] and then this source of carbon dioxide is removed before $CaCO_3$ dissolution takes place.

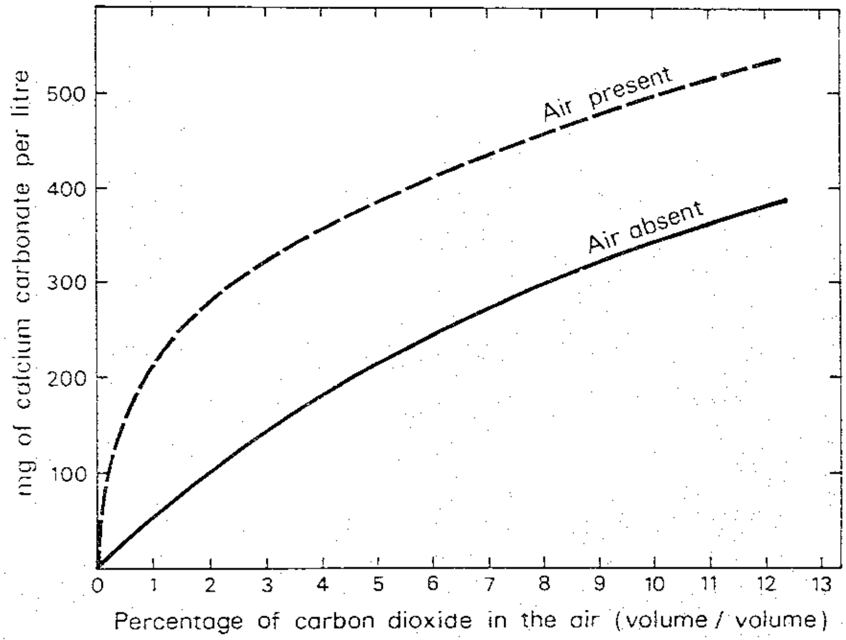

Figure 1.6. Water at 10°C is brought to equilibrium with air containing carbon dioxide and then the air is removed. The solid curve shows the amount of calcium carbonate (calcite) which can dissolve in this water. The broken curve shows the amount which can dissolve when air is always present. (After Picknett et al, 1976).

The reactions (1.8) to (1.11) move in a forward direction, so as the amount of $CO_{2(aq)}$ decreases ([H_2CO_3] decreases), there is no source of CO_2 to compensate for this loss and less $CaCO_3$ can dissolve than in the open system (Figure 1.6). Drake (1983) uses the terms coincident and sequential for the terms open and closed respectively. [$CO_{2(aq)}$] can be calculated as a function of PCO_2 in the coexisting gas phase by Henry's Law, where

$$(CO_{2(aq)}) = K_H.PCO_2 \qquad (1.26)$$

and, from Plummer and Busenberg (1982),

$$\log K_H = 108.3865 + .019T - 6919.53/T - 40.45154\log T + 669365/T^2 \quad (1.27)$$

where {T = T°C + 273.16°K}. As PCO_2 increases so does $[CO_{2(aq)}]$, however the temperature effect is inverse, so that the lower the temperature, the more carbon dioxide that can go into solution, e.g. at a given pressure if we assume 100% is in solution at equilibrium at 0.0°C, then at 30.0°C only 37.3% of the original amount is in solution at equilibrium (Figure 1.7).

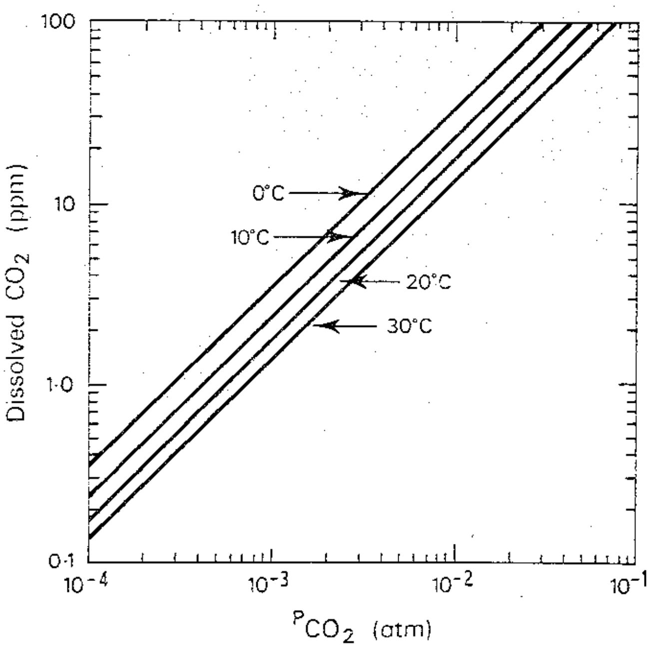

Figure 1.7. Solubility of carbon dioxide as a function of the CO_2 partial pressure in the coexisting gas phase. Calculated from the equilibrium constants in Table 1.1 using equation (1.20). (After White, 1988).

As noted by Bögli (1980, p.18) in his discussion on CO_2 on either side of the air\solution interface, "CO_2 is the only component in the $CO_2 - H_2O - CaCO_3$ system which can vary uninterruptedly within wide margins". The partial pressure of CO_2 varies considerably ranging from around 0.03-0.035% (normal atmosphere) to 0.03-1.0% (cave air) to 1.0-5.0% in the soil zone. The PCO_2 values given for the cave air and soil zone are the generally accepted range, although values of 1.0-6.0% (cave air; James, 1977) and 10.0-25.0% (soil zone; quoted in Bögli, 1980) are known to occur.

How do pH and calcium ion concentrations vary with changing PCO_2 values ? To evaluate this in the pure H_2O-CO_2 - $CaCO_3$ system at equilibrium, equations (1.15) to (1.19) and are rearranged so that,

$$K_{cal} = \{(Ca^{2+})K_1K_2K_{CO2}PCO_2\}/(H^+) \qquad (1.28)$$

Using the charge balance equation for electroneutrality to be satisfied (neglect ion pairs), (Drever, 1982; Dreybrodt, 1988; White, 1988),

$$[H^+] + 2[Ca^{2+}] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] \qquad (1.29)$$

for the region 6 < pH < 9, the charge balance equation reduces to,

$$2[Ca^{2+}] \approx [HCO_3^-] \qquad (1.30)$$

Using molar concentrations and ion activity coefficients (τ) and rearranging we find,

$$[Ca^{2+}]^3_{eq} = PCO_2.\{K_1K_{cal}K_{CO2}\}/\{4K_2\tau_{Ca2+}\tau^2_{HCO3-}\} \qquad (1.31)$$

and,

$$(H+)^3_{eq} = \{PCO_2\}^2\cdot\{K_1\}^2K_2\{K_{CO2}\}^2\tau_{Ca2+}\}/\{2K_{cal}\tau_{HCO3-}\} \qquad (1.32)$$

The solutions to which are plotted in Figure 1.8 for different temperatures.

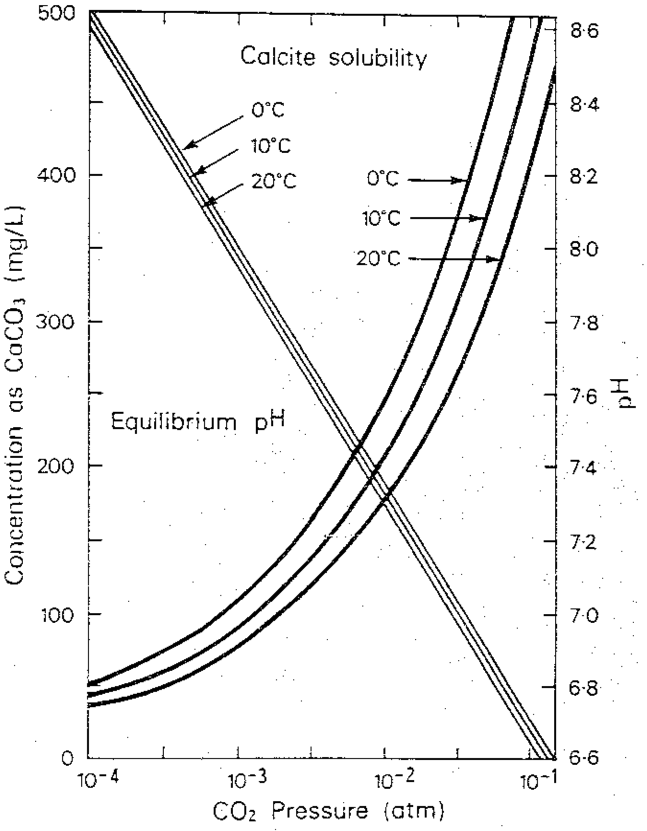

Figure 1.8. Solubility curves for calcite as a function of carbon dioxide partial pressure. Solubility curves were calculated from equation (1.31) using the equilibrium constants given in Table 1.1. At equilibrium, the saturated solutions will have the pH values shown as calculated from equation (1.32). (After White, 1988).

It must be remembered that these equations can be solved only for equilibrium in the open system, since PCO_2 remains constant during the dissolution process. For cases other than the open system one has to take into account the fact that PCO_2 decreases during dissolution, since for each Ca^{2+} molecule released into solution one molecule of $CO_{2(aq)}$ is consumed.

The higher CO_2 levels generally noted in the soil zone (10 - 100 times atmospheric level) are attributed to biogenic processes acting within the soil zone. The availability of this biogenic CO_2 allows rainwater that percolates through the soil zone to greatly increase its load of dissolved CO_2 (due to reaction **(1.15)**) and increase its aggressiveness to limestone and dolomite. It is this production of biogenic CO_2 and increase in the solutional power of percolating water that many researchers consider to be the overriding factor in carbonate dissolution (Smith and Atkinson, 1976; Woo and Marsh, 1977; Drake, 1980; Brook and Ford, 1982; Brook et al, 1983).

This percolating water, as is often the case in limestone terrains, on encountering a "new atmosphere" with a lower partial pressure of CO_2 (e.g. a cave) than that present in the soil zone, degases (i.e. CO_2 is given off) to re-establish equilibrium and this is usually accompanied by calcite precipitation as the resulting water is commonly supersaturated (Figure 1.9).

The equilibrium reactions given in this section give an overview of how the dissolution process of $CaCO_3$ may occur and by the use of such equations one can determine the maximum solubility of limestone and dolomite assuming equilibrium is established. These equilibrium reactions do not allow one to determine the actual quantity dissolved, in that these equilibrium reactions do not indicate how fast or how dependent particular reactions may be under different boundary conditions e.g. laminar or turbulent flow.

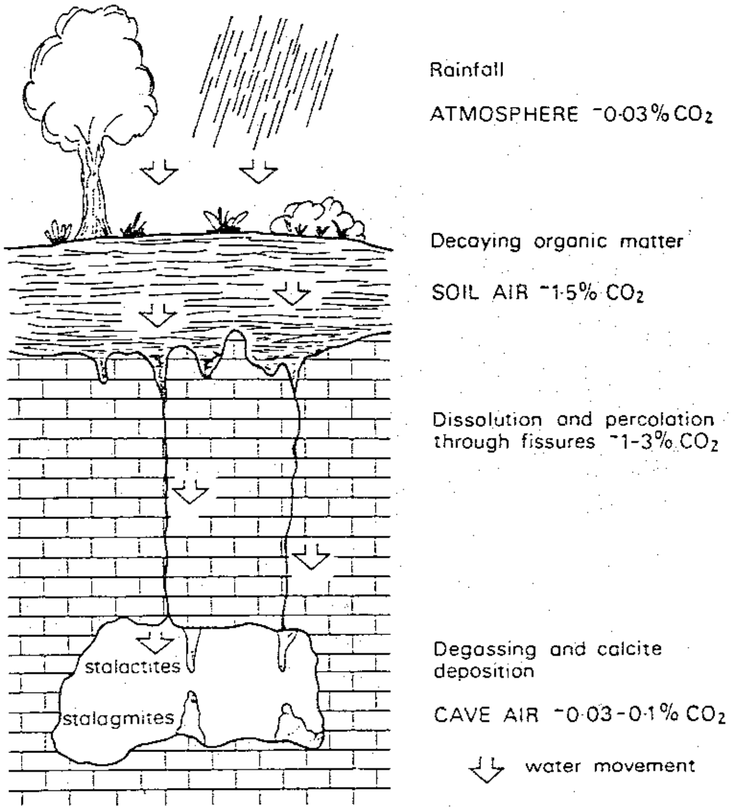

Figure 1.9. Model for the formation of calcite deposits in cave systems by degassing, the carbon dioxide being primarily derived from soil air. (After White, 1976).

CHEMICAL KINETICS AND TRANSPORT MECHANISMS

Rates of reactions (i.e. how fast does a particular reaction occur?) and transport mechanisms (i.e. movement of ions into and out of the bulk solution by convection or diffusion) are considered to be at least as important, if not more so, than equilibria factors in determining limestone solution and although it is beyond the scope of this thesis to describe these mechanisms in detail a brief outline of mechanisms involved is given here and more detailed discussions can be found in Roques (1969), Plummer et al (1978), Morse (1983), White (1984), Herman and White (1985), Buhmann and Dreybrodt (1985a, 1985b) and Dreybrodt (1988).

Dreybrodt (1988) considers that the dissolution of calcite is a complex process comprising three different simultaneously acting mechanisms,

1) Transport mechanisms - this step involves mass exchange between a liquid phase and a solid and requires some kind of transport mechanism, which in the case of dissolution removes ionic species released from the solid surface into the bulk of the fluid and vice versa for precipitation, without which dissolution and precipitation would not occur,

2) Kinetics of $CO_{2(aq)}$ - this step involves the kinetics of the conversion of $CO_{2(aq)}$ into the aggressive reactants H^+ and HCO_3^-. Dreybrodt (1988) considers this slow process is of the utmost importance since it can be the rate determining step, i.e. the rate of this reaction can control the rate of change of the whole system, especially in cases where the ratio of the solvent volume to the surface of the solid in contact

with the solvent is small. (White (1984) also considers the hydration of aqueous CO_2 to form H_2CO_3 to be a rate-limiting step and a critical parameter in surface karst processes. From White (1984), e.g. at $PCO_2 = 0.93$ atm, $[CO_{2(aq)}] = 0.029m$, whereas $[H_2CO_3] = 4 \times 10^{-5}$; the H_2CO_3 concentration is only 0.14% of $[CO_{2(aq)}]$, and,

3) Kinetics of calcite dissolution - this involves the kinetics of dissolution between the solvent and the solid phase. Plummer et al (1978) in their study of the chemical kinetics of calcite dissolution at various temperature and PCO_2 values found that the net dissolution rate (R) could be given by an equation of the form,

$$R = k_1(H^+) + k_2(H_2CO_3) + k_3(H_2O) - k_4(Ca^{2+})(HCO_3^-) \qquad (1.33)$$

with units of millimoles per centimetre square per second and where k_1, k_2 and k_3 are first order rate constants dependent on temperature, and k_4, the back reaction rate, is a function of both temperature and PCO_2. The term k_4 is a result of the interaction of Ca^{2+} and HCO_3^- species in the bulk fluid with surface speciation. From the above equation they concluded that the $CaCO_3$ dissolution process consisted of three simultaneous attacks at the calcite surface,

$$CaCO_3 + H^+ \Leftrightarrow Ca^{2+} + HCO_3^- \qquad (1.34)$$

$$CaCO_3 + H_2CO_3 \Leftrightarrow Ca^{2+} + 2HCO_3^- \qquad (1.35)$$

$$CaCO_3 + H_2O \Leftrightarrow Ca^{2+} + CO_3^{2-} + H_2O \qquad (1.36)$$

with the percentage contribution of each of these three mechanisms to the total forward rate varying depending on pH and PCO_2 values. For example, hydrogen ion attack (which can be visualised as reaction of calcite with a strong acid), **(1.34)**, is the dominant forward reaction at pH < 5.7 as a function of PCO_2 (25°C), with the carbonic acid attack, **(1.35)**, and the water reaction (physical dissolution of calcite in water), **(1.36)**, each being the dominant forward reaction under different conditions. At pH > 7 and PCO_2 <0.03 atm, i.e. the realm of most karst and natural waters, the reaction simplifies to,

$$R = k_3(H_2O) - k_4(Ca^{2+})(HCO_3^-) \qquad (1.37)$$

Buhmann and Dreydrodt (1985a, 1985b) in their study on the kinetics of calcite dissolution and precipitation under both open and closed conditions for both laminar and turbulent flow found that dissolution or precipitation rates could be approximated by a linear relationship,

$$R = \alpha\,([Ca^{2+}]_{eq} - [Ca^{2+}]) \qquad (1.38)$$

where α is a function of CO_2 pressure, thickness of the water film covering the $CaCO_3$ surface and temperature and $[Ca^{2+}]_{eq}$ is the Ca^{2+} ion concentration at equilibrium, and that under turbulent flow the rates are one order of magnitude higher than those for laminar flow.

Sjöberg and Rickard (1984a; 1984b) in their study of calcite dissolution kinetics looked at the dependence of the dissolution rate on temperature and pH in aqueous KCl solutions of 0.1 and 0.7 mole l^{-1} (concentration of total carbonate species normally < 10^{-5}). They found that the rate of dissolution of calcite could be described in terms of three pH regimes (Figure 1.10).

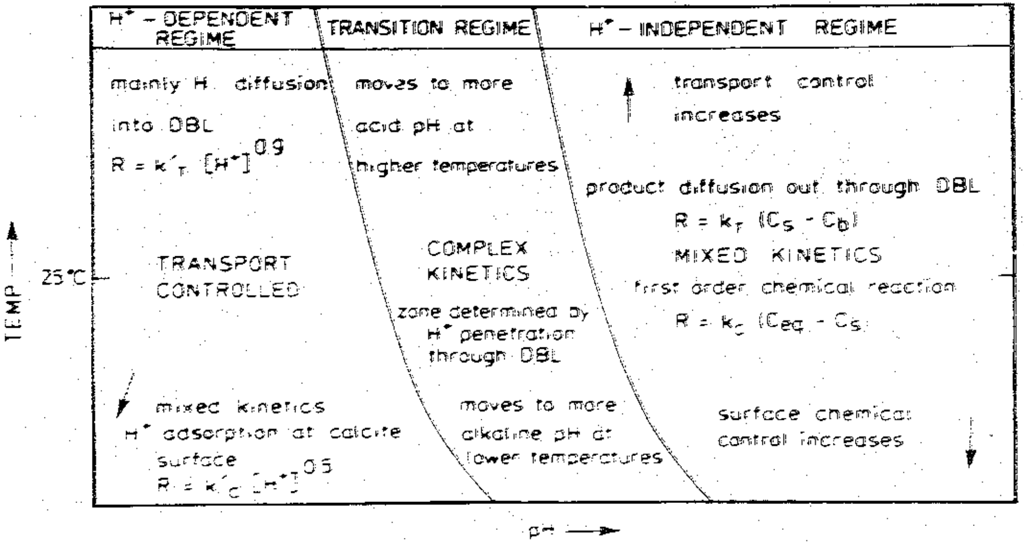

Figure 1.10. Summary of calcite dissolution kinetics depending on the pH of the solution and temperature. (After Sjöberg and Rickard, 1984a).

At low pH (< 4) at 25°C, the dissolution rate is almost proportional to $[H^+]$ and transport control dominates; for 4 < pH < 5.5 at 25°C a transition regime exists where $[H^+]$ dependence varies and for pH > 5.5 (25°C) the dissolution rate is independent of $[H^+]$ with mixed kinetics, as temperature increases transport control increases whereas if temperature decreases surface chemical control increases.

The solution kinetics of dolomite differ quite markedly from those established for calcite in that although its solubility at equilibrium is reasonably similar to that for calcite, equilibrium is achieved much more slowly (Drever, 1982; White, 1984). In their study on the dissolution kinetics of dolomite, Hermann and White (1985) found that the dissolution rate initially proceeds rapidly but as saturation increased the dissolution rate decreased, and at solution conditions still far from equilibrium (ion activity product = 10^{-19}) the dissolution rate dropped off sharply. They found that if they assumed this slow rate was constant for the rest of the reaction to reach equilibrium, the time required for IAP = K_{dol} (equilibrium) was of the order of 1 to 2 years (compared with the approximate ten to twenty-one days reported in the literature for calcite saturation to be achieved under laboratory conditions (Ford, 1988; White, 1988)).

It can be seen then that the process of the dissolution of limestone and dolomite is quite complicated and that one must be aware of the differing mechanisms involved that can operate under different chemical and hydrological conditions.

OTHER FACTORS AFFECTING LIMESTONE DISSOLUTION

Investigations by a number of researchers have shown that besides the equilibria and the kinetic-dynamic factors discussed other factors can enhance limestone (and dolomite) dissolution.

Thrailkill (1968) in his paper regarding cavern excavation in the "shallow phreatic zone" noted that undersaturation of previously saturated (with respect to calcite) vadose seepage waters could be achieved by, i) the mixing of warmer saturated seepage water with cooler phreatic water at the watertable, ii) the mixing of vadose seepage water with chemically dissimilar waters, and iii) floodwaters. The floodwaters he noted although maybe not directly involved in the dissolution process, could influence and enhance both the mixing and temperature effect by the floodwaters being cooler and having PCO_2 values closer to those for surface waters. These two effects are discussed below.

The mixing effect, termed "mischungskorrosion" (mixing corrosion) by Bögli (1964) results from an increase in the aggressiveness of a solution (solutional power) by the undersaturation of a solution, in this particular case, with respect to calcite, caused by the mixing of saturated waters with differing $CO_{2(aq)}$ content (Figure 1.11). Dreybrodt (1981) further discusses this "mixing corrosion" and its role in the karstification of limestone rocks.

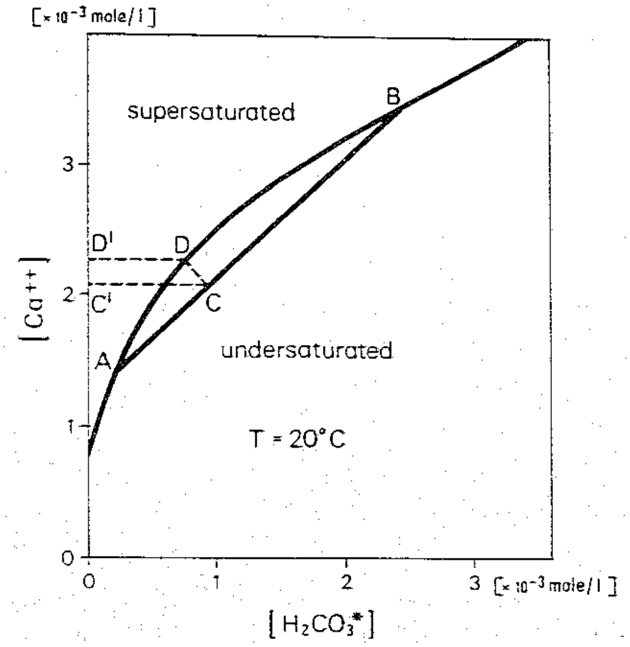

Figure 1.11. The equilibrium curve divides the $[H_2CO_3^*]$ - $[Ca^{2+}]$ diagram into two parts. Above the curve the solutions are supersaturated; below undersaturation exists. Mixing of two saturated solutions (A) and (B) leads to an undersaturated solution (C). The additional amount of Ca^{2+}, which can be dissolved after mixing is given by C^1D^1. (After Dreybrodt, 1988).

The temperature effect is due to the non-linear relationship between CO_2 and Ca^{2+} in solution in which the cooling of a solution, saturated or in equilibrium with calcite, at a given PCO_2 value requires less dissolved CO_2 for equilibrium to be achieved, i.e. additional CO_2 is available for calcite dissolution. Thrailkill (1968) calculated that when water at 11°C, in equilibrium with an atmosphere of $PCO_2 = 3 \times 10^{-3}$, is cooled to 10°C, in an open system with the same atmosphere, the extra amount of calcite dissolved is calculated to be 130 times the standard minimum undersaturation (standard minimum saturation = 0.0108 ppm Ca^{2+}). Bögli (1980) terms this temperature effect "cooling corrosion" and notes that in comparison with the mixing effect, the temperature effect is usually limited to the uppermost meters of the rock as below a certain depth groundwater will in most cases be at the mean annual temperature.

As well as the temperature and mixing effects that can occur when carbonate waters mix, the chemical composition of the mixing waters can also be important in either enhancing or hindering the dissolution and precipitation processes (Runnells, 1969; Picknett et al, 1976; Jakucs, 1977; Drever, 1982). Laboratory work by Akin and Lagerwerff (1965a; 1965b), Roques (1969), Picknett (1972) and Picknett and Stenner (1978) has shown that the introduction of solutions containing foreign salts (e.g. NaCl, $MgCl_2$ and $CaSO_4$) into the $CO_2 - H_2O - CaCO_3$ system causes shifts in calcite equilibrium, which depending on the salt added and its concentration, can either enhance or reduce calcite solubility.

The common ion effect (in which a substance, or substances in solution have an ion in common with the carbonate system, Ca^{2+} or CO_3^{2-}) reduces calcite solubility because of changes in the solubility product caused by an increase in the concentration of the common ion, e.g. the addition of a $CaCl_2$ solution reduces calcite solubility because of the increase in Ca^{2+} ions.

The ionic strength effect (in which a substance, or substances in solution has no ion in common with the carbonate system) increases calcite solubility due to an increase in the ionic strength of the final solution resulting in a decrease in ion activities and hence to satisfy equilibrium conditions more calcite must dissolve, e.g. the addition of a NaCl solution. Calcite solubility is nearly doubled in seawater when compared to freshwater at the same temperature and PCO_2 value. According to Picknett et al (1976) ion-pairing can also enhance calcite solubility through the effect of the ion-pairs on ionic strength. White (1988) lists the following ion-pairs as being of the most importance to carbonate groundwaters,

$CaHCO_3^+$, $MgHCO_3^+$, $CaCO_3^o$, $MgCO_3^o$, $CaSO_4^o$ and $MgSO_4^o$.

The common ion effect and the ionic strength effect of foreign ions in solution on limestone solubility are best determined by using a general charge equation (Drever, 1982), involving the ions commonly found in natural water systems (neglect minor species),

$$\underbrace{(m_{Na^+} + m_{K^+} + 2m_{Mg^{2+}} - m_{Cl^-} - 2m_{SO_4^{2-}})}_{M} + 2m_{Ca^{2+}} = m_{HCO_3^-} + 2m_{CO_3^{2-}} \qquad (1.39)$$

Drever (1982) termed the first five variables, M, and showed that if M is positive the amount of Ca^{2+} in equilibrium with calcite is decreased (common ion effect), and if M is negative the amount of Ca^{2+} in equilibrium increases (ionic strength effect).

Trace metals such as Pb^{2+}, Cu^{2+}, Sc^{2+} and Mn^{2+} have been shown to inhibit limestone solubility (Terjesen et al 1961; Nestaas and Terjesen, 1969). Buhmann and Dreybrodt (1987) in their continuing work on the dissolution kinetics of calcite found that although foreign ions can displace calcite solution equilibria (by ionic strength, ion-pairing and common ion effects) the kinetics of the dissolution process were virtually unchanged. Further work by them on the kinetics of calcite dissolution using four different limestone samples and a white marble sample (all > 95% $CaCO_3$), also showed that the effect of lithology, i.e. the chemical composition, on dissolution rates were also very minor.

It is important to remember that the equilibria and rate constants are mostly derived from experiments under controlled conditions in laboratories and that in the "real world" boundary conditions and purity of minerals etc., can vary quite markedly even within quite small (< $1km^2$) areas of carbonate rock.

CARBONATE PRECIPITATION

Carbonate deposition (predominantly as calcite or aragonite) within caves found in limestone and dolomite regions is a well known phenomenon occurring world wide. The deposition and formation of the many different types of speleothems found in the cave environment (see Hill and Forti, 1986) is predominantly attributed to the rapid outgassing of CO_2 from water containing a high dissolved load of $CaCO_3$ issuing from joints and fissures. (This of course assumes that the issuing water contains a higher concentration of dissolved CO_2 than that corresponding to the PCO_2 level of the cave atmosphere, i.e. $PCO_{2(w)} > PCO_{2(a)}$). Evaporation leading to an increase in concentration and the oversaturation of Ca^{2+} and dissolved CO_2 (which in turn causes CO_2 to be given off) can also play a role in $CaCO_3$ deposition (Bögli, 1980).

Atkinson (1983) in his study of actively growing calcite speleothems beneath a high alpine terrain and active glaciers (Castleguard Cave, Canada) however found that calcite precipitation by CO_2 degassing, temperature effect and evaporation was minimal. Supersaturation and the precipitation of calcite resulted mainly from common-ion effects (an increase in the Ca^{2+} ion concentration was bought about by the oxidation of pyrite to sulphuric acid with increased dissolution of calcite and dolomite).

Supersaturation or an increase in the degree of supersaturation of a particular water is achieved by the re-establishing of equilibrium under new boundary conditions (e.g. new atmosphere of lower PCO_2 levels) and as these new equilibrium conditions are met "excess" $CaCO_3$ precipitates out of solution (Figure 1.12). This precipitation of $CaCO_3$ can best be summarised by the overall reaction,

$$Ca^{2+} + 2HCO_3^- <=> CaCO_{3(solid)} + H_2O + CO_{2(gas)} \quad (1.40)$$

In which the first step is the degassing of CO_2 according to the reaction,

$$H^+ + HCO_3^- <=> H_2CO_3 <=> H_2O + CO_{2(gas)} \quad (1.41)$$

and as a consequence the solution becomes progressively supersaturated with respect to $CaCO_3$, with a rise in pH also being noted due to the consumption of H^+ ions. At higher degrees of supersaturation $CaCO_3$ will nucleate,

$$Ca^{2+} + CO_3^{2-} <=> CaCO_{3(solid)} \quad (1.42)$$

and precipitation and degassing occur simultaneously (overall reaction). Using the equations on page 11 and the data given in Table 1.1, a measure of the saturation state of a particular solution can be determined. For equilibrium to be established between the solid phase (mineral phase) and the ions in solution, say for calcite,

$$K_{cal} = (Ca^{2+})_{eq}(CO_3^{2-})_{eq} \quad (1.43)$$

where K_{cal} is the solubility product for calcite and $(Ca^{2+})_{eq}$ and $(CO_3^{2-})_{eq}$ are the respective ion activity's at equilibrium.

Two numerical ways of expressing the "equilibrium state" of a solution have been presented in the

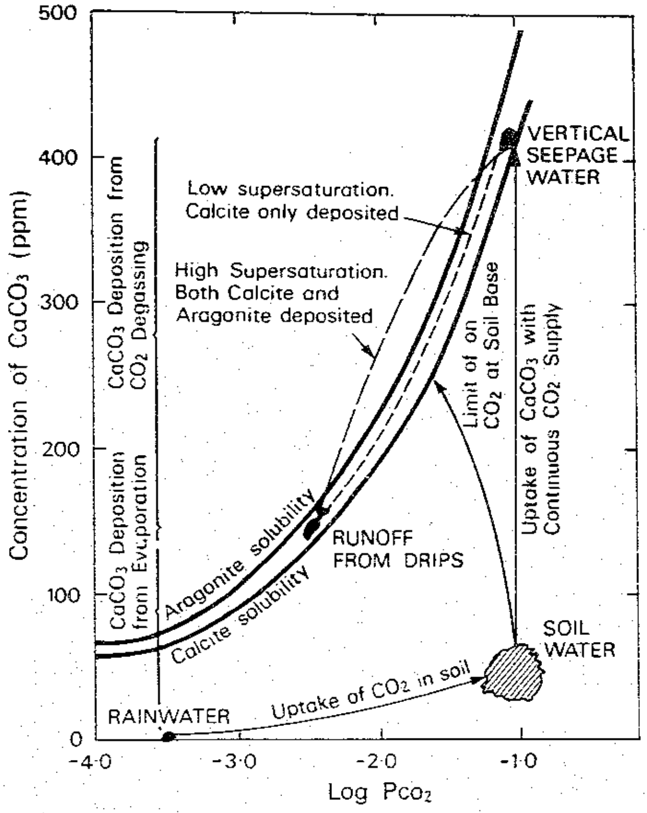

Figure 1.12. Changes in the chemical composition of water (rain) entering into the soil where CO_2 uptake is effected. During vertical seepage in the rock $CaCO_3$ is dissolved under open or closed system conditions. Supersaturation in the cave develops by outgassing of CO_2 and further by evaporation of water. (After White, 1976).

literature (calcite will be used an example),

$$S_{cal} = IAP/K_{cal} = (Ca^{2+})_{aq}(CO_3{}^{2-})_{aq}/K_{cal} \tag{1.44}$$

solution is undersaturated with respect to calcite for $S_{cal} < 1$, at equilibrium with respect to calcite for $S_{cal} = 1$ and supersaturated with respect to calcite for $S_{cal} > 1$, and

$$SI_{cal} = \log\{IAP/K_{cal}\} = \log\{(Ca^{2+})_{aq}(CO_3{}^{2-})_{aq}/K_{cal}\} \tag{1.45}$$

solution is undersaturated with respect to calcite when SI_{cal}, saturation index for calcite, < 0, saturated with respect to calcite when $SI_{cal} = 0$ and supersaturated with respect to calcite for $SI_{cal} > 0$. Note for both cases $(Ca^{2+})_{aq}(CO_3^{2-})_{aq}$ = IAP (ion activity product). The logarithmic scale provides equal intervals between equal degrees of either undersaturation and supersaturation (White, 1988) and is used in preference throughout this thesis unless otherwise noted.

$CaCO_3$ does not necessarily precipitate immediately once supersaturation is reached; Plummer et al (1978) have shown that nucleation is slow and crystallisation is kinetically inhibited, and until these kinetic inhibitions on calcite precipitation are overcome precipitation will not occur. Reddy (1977) in his study on calcite seed growth found that PO_4^{2-} ions could inhibit calcite crystallisation by adsorption onto the nuclei surface at active growth sites. Excellent reviews on the kinetics of calcite precipitation can be found in Morse (1983) and Dreybrodt (1988).

Processes or effects that may govern carbonate precipitation such as the role of turbulence or the presence of aquatic biota are discussed in more detail in Chapter Seven.

CARBONATE WATERS

The hydrologic cycle for fluviokarst drainage basins can be summarised by the diagram in Figure 1.13, in which it is assumed that the karst aquifer and associated groundwater basins are embedded in a larger basin containing non-karstic rocks. Using the idealised end-members proposed by White (1969), carbonate aquifers can be classified according to their hydrogeological properties into three main types with a number of sub-types (Table 1.2).

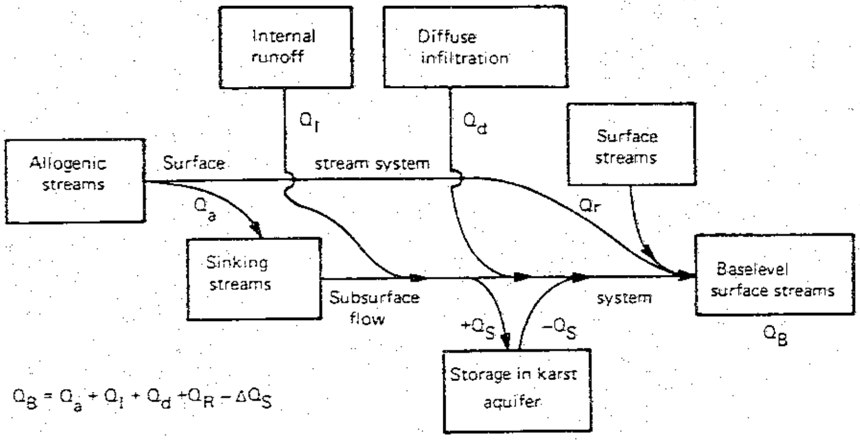

Figure 1.13. Water balance for a fluviokarst drainage basin. (After White, 1988).

The main types are, i) Diffuse flow, ii) Free flow, and iii) Confined flow aquifers (Figure 1.14). In diffuse flow aquifers a well defined water table is present, solutional enlargement of joints etc. is limited and flow obeys or nearly obeys Darcy's Law (laminar flow) and discharge is through a large number of small springs and seeps.

In free flow aquifers, water moves through well developed and integrated conduits under the influence of gravity and integrated conduits under the influence of

TABLE 1.2. TYPES OF CARBONATE AQUIFER SYSTEMS IN REGIONS OF LOW TO MODERATE RELIEF. (AFTER WHITE, 1969).

FLOW TYPE	HYDROLOGICAL CONTROL
I. DIFFUSE FLOW	GROSS LITHOLOGY Shaly limestones; crystalline dolomites; high primary porosity.
II. FREE FLOW	THICK, MASSIVE SOLUBLE ROCKS
a) PERCHED	Karst system underlain by impervious rocks near or above base level.
1. OPEN	Soluble rocks extend upward to level surface.
2. CAPPED	Aquifer overlain by impervious rock.
b) DEEP	Karst system extends to considerable depth below base level.
1. OPEN	Soluble rocks extend to land surface.
2. CAPPED	Aquifer overlain by impervious rocks.
III. CONFINED FLOW	STRUCTURAL AND STRATIGRAPHIC CONTROLS
a) ARTESIAN	Impervious beds which force flows below regional base level.
b) SANDWICH	Thin beds of soluble rock between impervious beds.

gravity and turbulent flow is often achieved; conduit gradients are generally low and the water table may be essentially horizontal for long distances despite irregularities in the topography; discharge is often through large springs, usually consisting of a single outlet, which can accumulate water flowing through vast areas of underground drainage. Confined flow aquifers are those in which recharge to the aquifer is restricted beneath impermeable confining beds and water movement is dictated by responses in hydrostatic pressure.

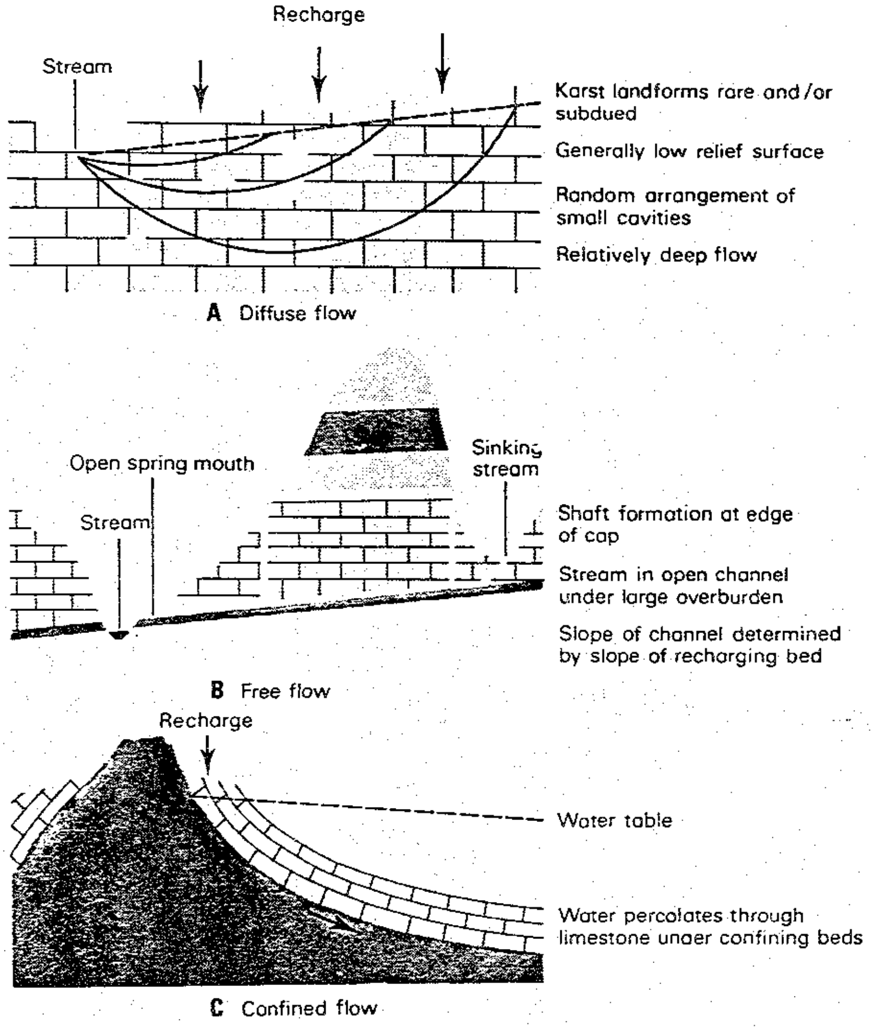

Figure 1.14. Classification of flow types in karst aquifers. (After White, 1969).

KARST SPRINGS

There exists in the literature a confusing array of "karst spring categories" that have been used for classification. In this section an overview will be presented of these karst spring categories in order to determine which of these "classifications" best determines spring type for the karst springs found in the study area examined in this thesis. Study area details are presented in Chapter Two.

For the majority of limestone and dolomite regions, karst springs, or risings, represent the downstream outlet for recharge to carbonate aquifers. These karst springs predominantly occur at the interface between surface and subsurface environments where water derived from either autogenic or allogenic sources, returns to the surface (Figure 1.15). (Autogenic = any recharge to the system is totally derived from within the carbonate catchment; Allogenic = recharge to the system is derived from non-carbonate sources which usually sink on reaching carbonate rocks).

Karst springs occur in a variety of forms (see Sweeting, 1973; Bögli, 1980; Jennings, 1985), with most types fitting into the three general classifications used by Myrolie (1984). These are :-

i) Gravity Springs - these are springs where water under gravity leaves the subsurface following a down-slope gradient and where the actual opening may be partially blocked by collapse or colluvium,

ii) Artesian Springs - these are springs in which water flows from a confined aquifer due to a hydrostatic pressure gradient and not a down-slope gradient; included in this type are vauclusian and alluviated springs, and

iii) Overflow Springs - these are simply springs that are only activated under high flow (flood) conditions, where the volume of discharge is too great for the normal spring to cope with. Depending upon passage characteristics, overflow springs can be either gravity or artesian springs.

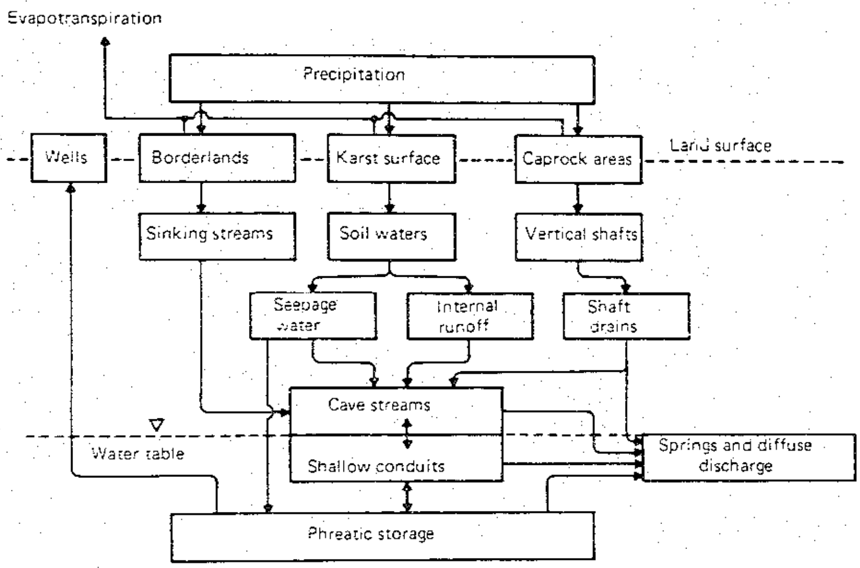

Figure 1.15. Internal flow system of a karst aquifer. (After White, 1988).

Karst springs can also be classified according to the origin of the waters they discharge, i.e. autogenic or allogenic inputs can be used to differentiate between karst springs occurring in a particular karst area, and according to the classification given by Bögli (1980) they are,

i) emergence - larger karst springs without further evidence of the origin of the water,

ii) resurgence - the re-emergence of a swallet stream at the surface, (equivalent to allogenic), and

iii) exsurgence - autochthonous seepage water flowing out (equivalent to autogenic).

Jennings (1985) uses only the terms exsurgence (spring fed entirely by seepage through karst rocks) and resurgence (spring where a former surface stream re-appears, assumed to be flowing over non-carbonate rocks) as a means of classifying spring types, although he carefully notes that karst springs exist that represent every stage of transition between these two end-members. Lauritzen (1981) in his study of 87 karst springs in Norway, divided springs into either resurgences or exsurgences, depending upon the origin of the spring waters (see Figure 1.16 for more details).

Physical parameters (e.g. storm and baseflow hydrographs, water temperature, visible water tracers, conductivity, etc.), chemical parameters (e.g. concentrations of Ca^{2+}, HCO_3^-, water tracers, etc.) and computed parameters (log PCO_2, saturation indices of calcite and dolomite, coefficient of variation of total hardness, etc.) derived from measurements made on water samples collected from autogenic percolation systems and karst springs, have also been used by many researchers as a means of classifying the recharge and discharge characteristics of carbonate aquifers (Thrailkill, 1968; Shuster and White, 1971; Ede, 1975; Atkinson, 1977a, 1977b; Williams and Dowling, 1979; Cowell and Ford, 1980;

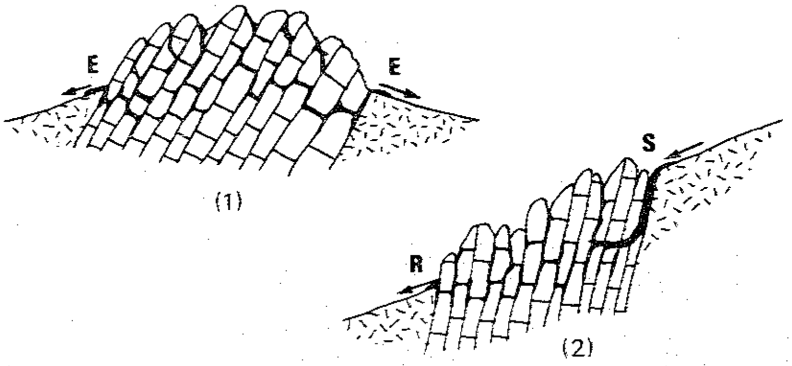

Figure 1.16. Karst drainage types in geological settings that are typical for the cases found in Norway.

1) Autogenic karst drainage - The whole catchment area is in limestones, and the springs are consequently fed by limestone infiltration only. Water emerges as "exsurgences" (E).

2) Allogenic karst drainage - Water from non-limestone catchments enter the limestone through "sinkholes" (S) and reappear in "resurgences" (R). The autogenic infiltration is diluted by the allogenic input. (After Lauritzen, 1981).

Thrailkill and Robl, 1981; Williams, 1983; Crowther and Pitty, 1982; Crowther, 1983; Krothe and Libra, 1983; Troester and White, 1986; Scanlon and Thrailkill, 1987; Crowther, 1989).

For example, on the basis of hydrogeologic evidence Shuster and White (1971) classified a number of carbonate springs into either diffuse-flow feeder systems or conduit feeder system types (the two end-members of their classification). These two classifications are from White (1969). They also compared, over a year long period, variability of carbonate hardness, fluctuations in spring water temperature and the saturation index with respect to calcite, and found that the springs they sampled on the basis of the above parameters fell into either of one of the two types. The diffuse flow springs showed little seasonal variation in carbonate hardness, i.e. the coefficient of variation of total hardness was < 5.0%, the springs were on average near saturation and generally warmer with small fluctuations in water temperature. On the other hand, conduit flow springs were very variable in terms of hardness values throughout the study (coefficient of variation of carbonate hardness 10 - 24%), they were always undersaturated with respect to calcite and showed larger fluctuations in spring water temperatures than noted for the diffuse flow springs. In their discussion on the use of chemical data to characterise spring types they noted that the classification of a spring into the diffuse flow category was not as straight forward as for classifying conduit flow springs.

Using the diffuse flow - conduit flow end-members proposed by White (1969), Atkinson (1977a, p.108) in his study of the hydrogeology of the Carboniferous Limestone of the Mendip Hills concluded that "limestone aquifers are two-component systems in which the majority of storage is in the form of true groundwater found in narrow fissures, where laminar flow prevails, but the majority of water is transmitted through the rock by turbulent flows in solutionally enlarged conduits".

Krothe and Libra (1983) used sulphur isotope data as well as hydrological and geochemical data to classify springwaters as diffuse (deep) flow, conduit (shallow) flow or mixed flow (based on Shuster and White, 1971) in their study of flow systems in the karst terrain of southern Indiana. Scanlon and Thrailkill (1987) on the other hand, in their study of spring types in the Inner Bluegrass Karst Region of Kentucky, found that although dye-tracing experiments identified two physically distinct spring types (local high-level springs which discharge from shallow flow paths and major low-level springs which discharge from deep integrated conduit flow systems) the use of spring water chemistry or seasonal variations in spring water chemistry could not distinguish between the two spring types. They attributed the chemical similarities noted between the two spring types to the fact that recharge of the major low-level springs is from both percolation and high-level spring discharge and that most chemical reactions occur near the recharge zone. In comparing spring characteristics found in their study with those found by Shuster and White (1971) in Pennsylvania they concluded that (p.277), "the differences in relationships between chemical and physical attributes of springs in the Inner Bluegrass and Pennsylvania reflect fundamental differences in bedrock geology and structure".

Hence, it can be seen that aquifer and spring characterisation can be achieved by a variety of physical and chemical techniques, preferably used in conjunction with one another and that geological and structural controls on a particular karst system can greatly influence spring characteristics. In this thesis spring waters from a small karst area will be analysed and discussed in this context.

The hydrochemistry of karst springs and the characterisation of water feeding these springs has been reasonably well documented for karst systems in the northern hemisphere (Jacobson and Langmuir, 1970; Paterson, 1971; Gunn, 1974; Atkinson, 1977b; Cowell and Ford, 1980; Jawad and Hussein, 1986), whereas detailed temporal studies of the physical and chemical properties of karst spring waters are virtually non-existent for Australian karst areas. The exceptions are the long term study by Jennings (1972a; 1972b; 1983) in southeastern New South Wales and the study by Goede (1973) in southwestern Tasmania.

Other studies of karst waters from the different limestone areas of Australia (Sweeting, 1960; Jennings, 1963; Jennings and Sweeting, 1963; Handel and James, 1977; Dunkerley, 1981; James et al, 1982; Jennings, 1982; Houshold, 1984; Dunkerley, 1987) have usually been based on only a limited number of water samples from individual sites (mainly due to time constraints or the inaccessibility of particular karst areas at certain times of the year). Recent evidence presented by McMahon (1982), Finlayson et al (1986) and Finlayson and McMahon (1988) demonstrates that Australian rivers have a higher variability of annual flow and more extreme flood behaviour than streams in other continents with the exception of Southern Africa, so a knowledge of the temporal variability of discharge and the chemical composition of Australian karst springs is of prime importance when calculating denudation rates and for comparing karst spring data from one karst area to another.

OUTLINE OF THIS STUDY

The Buchan limestone area provides an ideal site to investigate the temporal and spatial variability of karst waters for an area in which very little information regarding the chemical composition of carbonate and non-carbonate waters is available. Details of the geology, hydrology and climate of the study area are presented in Chapter Two. In Chapter Three sampling procedures and physical and chemical methods of analysis are described with the results of these analyses being presented in Chapter Four. In Chapters Five and Six spatial and temporal variability of the sites sampled are looked at as well as spring water classification. Deposition of $CaCO_3$ (as tufa) at spring sites is discussed in Chapter

Seven, and Chapter Eight summarises results and trends found.

CHAPTER TWO

STUDY AREA

INTRODUCTION

The study area lies in the southern part of the Eastern Highlands of Victoria, Australia, some 350km east of Melbourne (Figure 2.1). It is an area of strong relief where dissected uplands flank either side of a broad open north-south trending intermontane basin (L.C.C., 1982). This basin (2-10km wide and 20km long) has been eroded in the limestones and mudstones of the Buchan Group and is surrounded by rhyolitic volcanics. The study area is the largest of a number of karst barrés in the Eastern Highlands (Figure 2.1). A karst barré is a area of limestone completely surrounded by impermeable rocks across which the output of the karst area must pass to reach general base level i.e. geomorphological development is dependent upon the variations in base level within the surrounding impermeable rocks (Sweeting, 1973; Bögli, 1980). Jennings (1985) uses the term impounded karst synonymously with the term karst barré.

GEOLOGY AND GEOLOGICAL HISTORY

The oldest rocks in the area are a thick sequence of metamorphosed Middle to Late Ordovician marine sediments forming the Wagga (or Omeo) Zone (Figure 2.2), which is

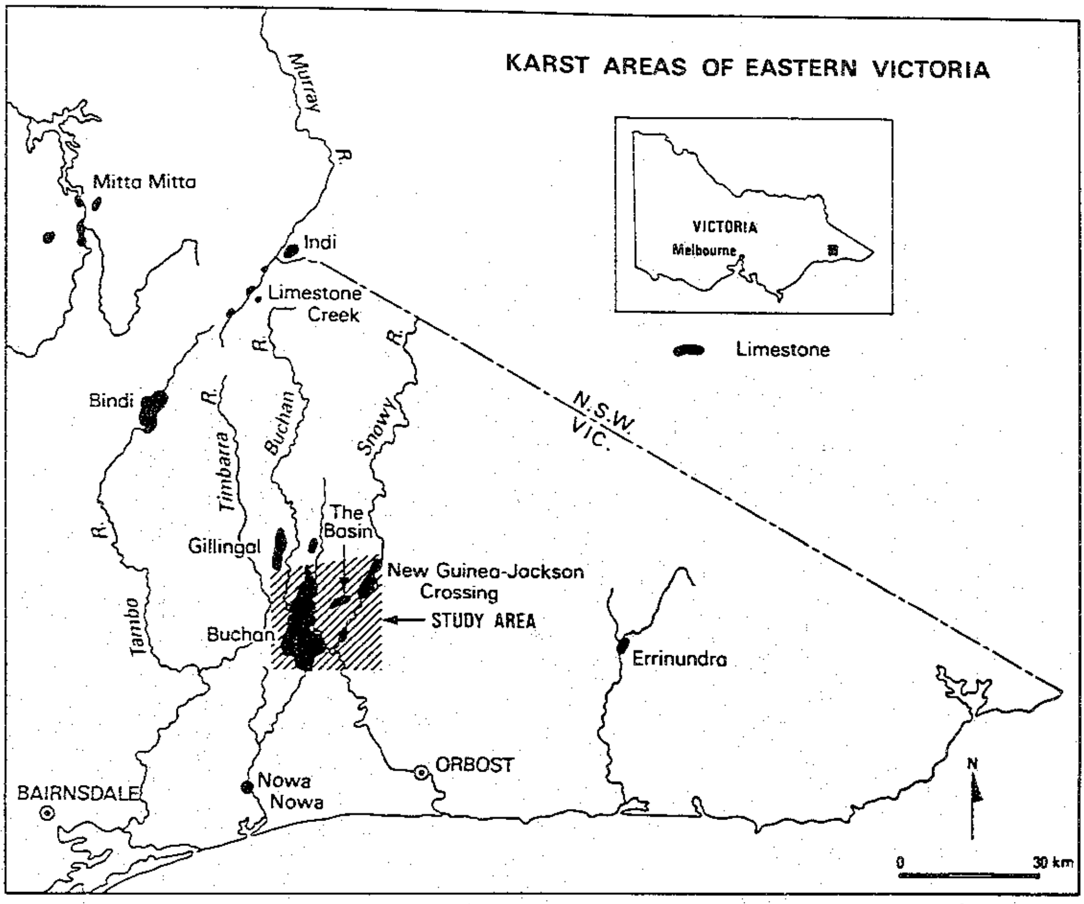

Figure 2.1. Study area location and karst barrès of eastern Victoria (After Fabel, 1987).

part of the Lachlan Fold Belt (Talent, 1969; Vandenberg and O'Shea, 1981; Cas, 1983). During the Benambran Orogeny (Early Silurian) these sediments were tightly folded and subjected to localised high-temperature metamorphism and granite intrusion.

Further deposition of marine sediments occurred in the Late Silurian, and these strata were folded prior to the extrusion of acidic volcanics (Thorkidaan Volcanics) which in turn were deformed and faulted during the Early Devonian. Vandenberg and O'Shea (1981) ascribe both these

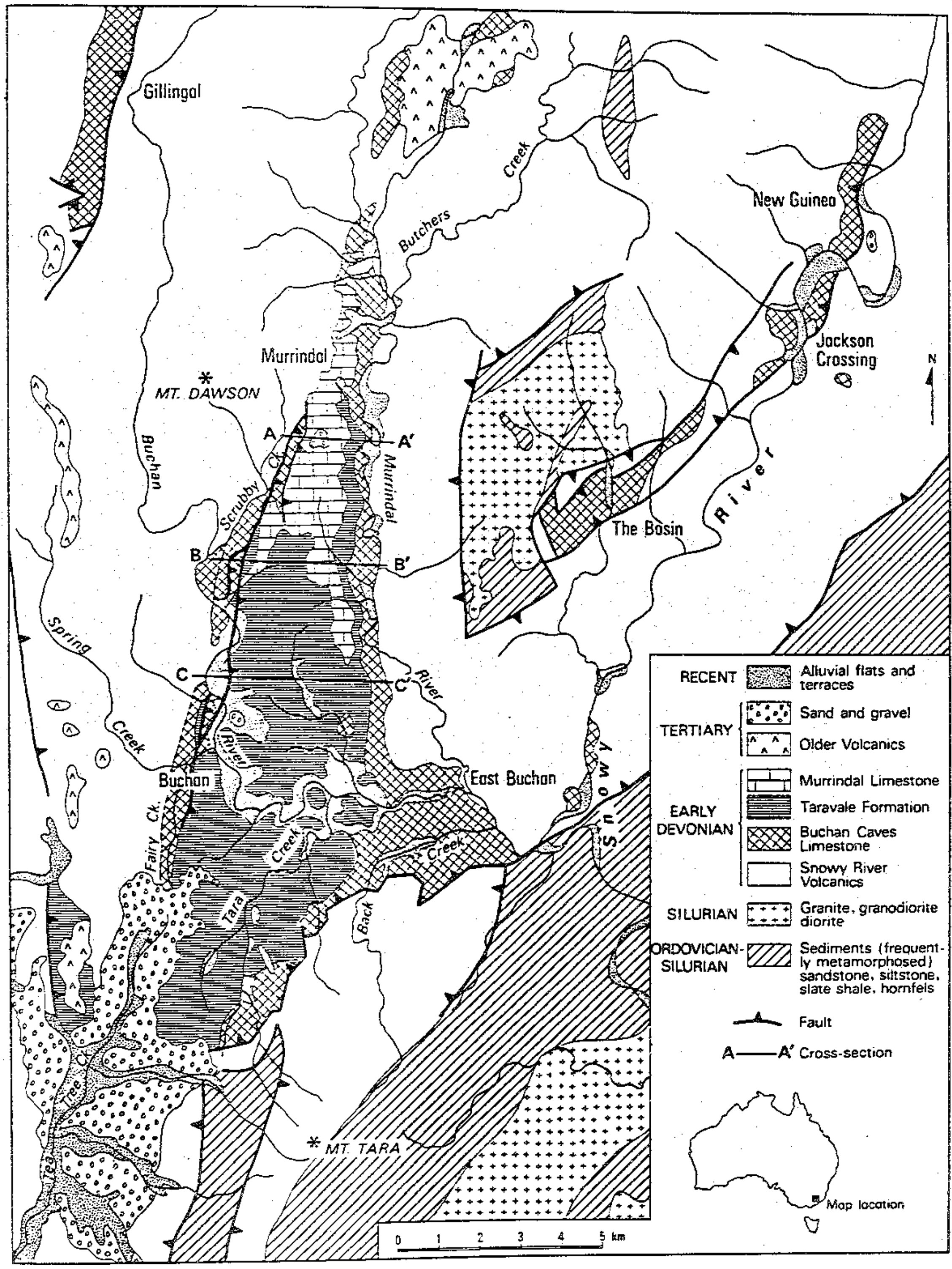

Figure 2.2. Geology of the study area (After Teichert and Talent, 1958).

periods of deformation to the Bowning Orogeny.

Prior to the widespread deposition of the shallow marine carbonates of the Buchan Group there was a period of widespread sub-aerial acidic volcanism (Snowy River Volcanics). According to Vandenberg (1976) the Snowy River Volcanics either overlie unconformably, or are faulted against all older rocks. The Snowy River Volcanics underlie and surround the Buchan Group carbonate rocks throughout the study area (Figures 2.2 and 2.3). The Snowy River Volcanics are a thick (3,000m at Buchan) and stratigraphically complex sequence of predominantly ignimbritic acid volcanics (rhyolite and rhyodacite with minor intermediate rocks) interbedded with fluviatile sediments including volcanogenic conglomerates, arkosic sandstones and occasional shales (Fletcher, 1963; Vandenberg and O'Shea, 1981).

THE BUCHAN GROUP

The Early Devonian (Emsian; Mawson, 1987) limestones and mudstones of the Buchan Group are preserved in a large, north-south trending synclinal belt between Murrindal, Buchan and East Buchan (Figure 2.2), in a large half-graben at Bindi (north of the study area) and in smaller grabens at Gillingal, The Basin and the Jacksons Crossing-New Guinea Ridge area; there are also smaller patches elsewhere (Teichert and Talent, 1958;

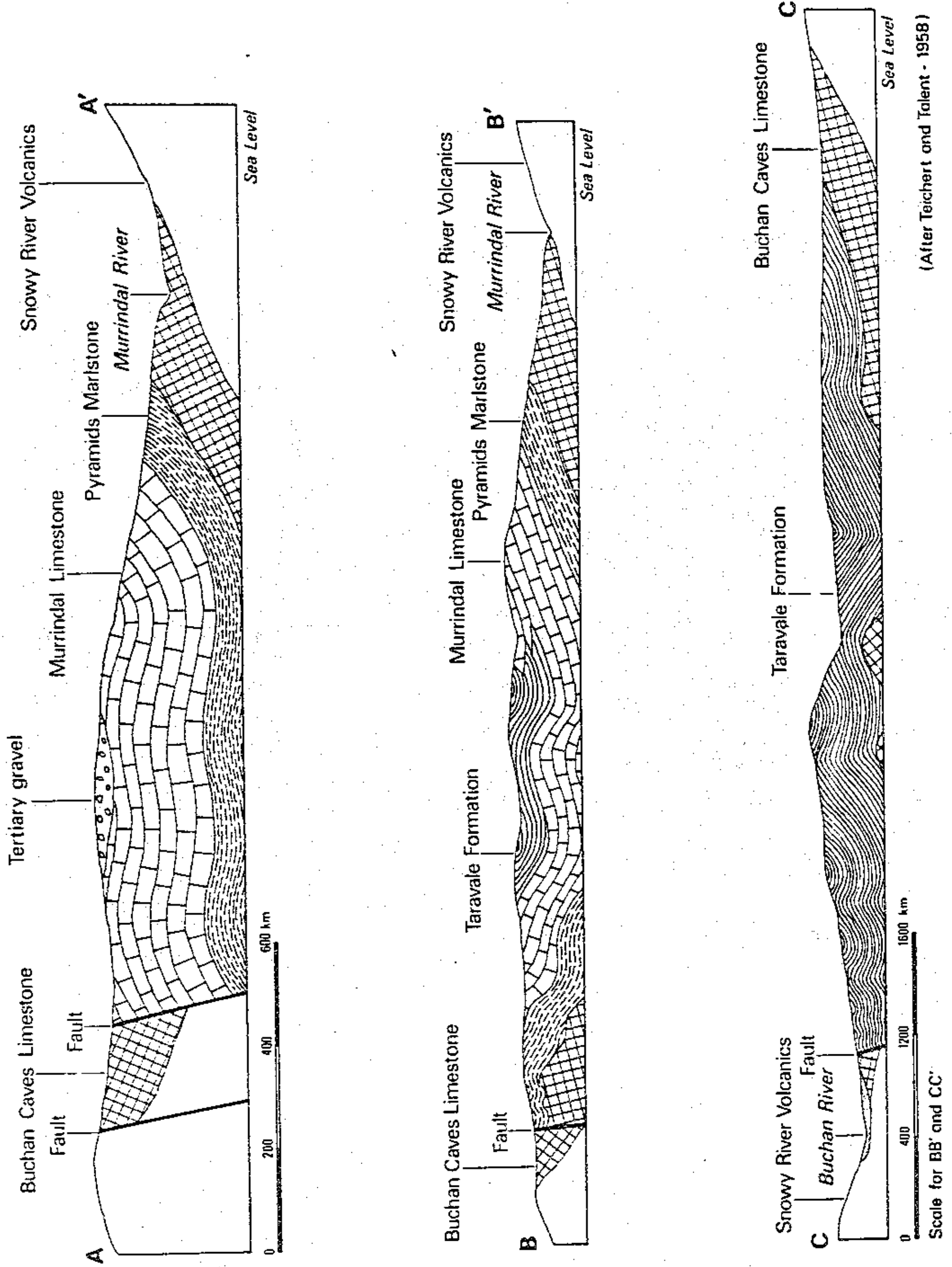

Figure 2.3. Cross sections AA', BB' and CC' from figure 2.2.

Vandenberg and O'Shea, 1981). The Buchan Group is composed of three main subunits: i) the Buchan Caves Limestone, ii) the Taravale Formation, and iii) the Murrindal Limestone (Teichert and Talent, 1958). The

Taravale Formation is known only from Bindi and Buchan-Murrindal, while the Murrindal Limestone occurs only at Murrindal.

The oldest of the three main subunits, the Buchan Caves Limestone, disconformably overlies the Snowy River Volcanics (Husain, 1981) and reaches a maximum thickness of 423m just south of Buchan (Cockbain, 1970). Around the margins of the Buchan Synclinorium this limestone unit is somewhat thinner (see cross-sections in Figure 2.3). The Buchan Caves Limestone unit begins with the lenticular Spring Creek Member, which consists of massive sandstone, volcanic breccia and interbedded sandstone-mudstone (Orth, 1982). Deposition of the Spring Creek Member changed from non-marine to marine as the main transgression became established, and it is overlain by poorly fossiliferous dolomite and dolomitic limestone which grade upwards into fairly pure limestone (Teichert and Talent, 1958; Cockbain, 1970). Chemical analyses of seventy-five Buchan Caves Limestone samples by Jenkin and Baxter (1968) gave values ranging from 51.9% $CaCO_3$ and 42.8% $MgCO_3$ (dolomite) to 96.5% $CaCO_3$ and 1.4% $MgCO_3$ (limestone). The Buchan Caves Limestone was deposited in very shallow intertidal conditions, probably largely as mudflats dominated by blue-green algae (Pilapil, 1987).

The Taravale Formation conformably overlies the Buchan Caves Limestone throughout most of the Buchan area. The basal portion of the Taravale Formation is often differentiated as the Pyramids Marlstone, which consists of thin beds of calcareous mudstone and fossiliferous calcareous nodules (100m thick at Buchan). The Taravale Formation itself (808m thick at Buchan) is a sequence of mudstones, shales and impure limestones which occupies most of the southern part of the Buchan Basin. Towards the north, this unit interfingers with the Murrindal Limestone, and also partly underlies it as the Pyramids Marlstone (Figure 2.4).

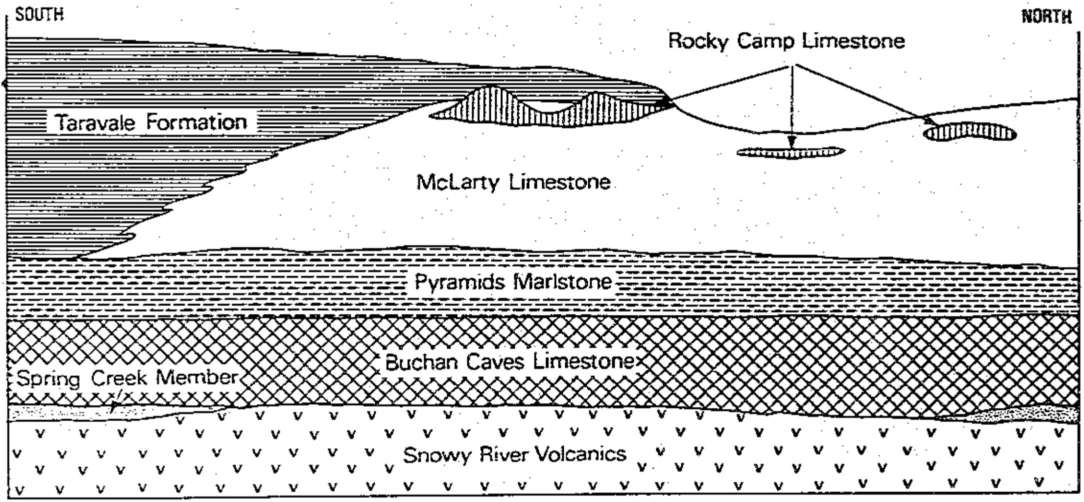

Figure 2.4. Diagram showing the relationships between stratigraphical units of the Buchan Group.

The Murrindal Limestone is divided into two members (Figure 2.4). The McLarty Member comprises 60-190m of well-bedded dark grey limestone while the upper Rocky Camp Member consists of 60-100m of light grey massive limestone containing a variety of well preserved fossils.

Wallace (1982) was able to show that the Rocky Camp Member was deposited as a large carbonate bank, facing the open ocean to the south, where the Taravale Formation accumulated. Behind the bank to the north, was a shallow lagoonal environment now represented by the McLarty Member (Figure 2.5).

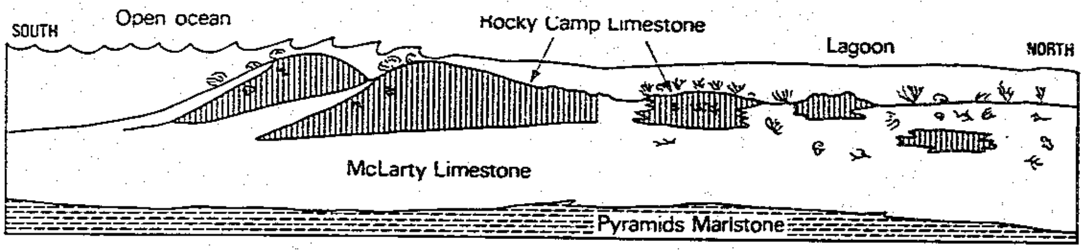

Figure 2.5. A reconstruction of the environments of deposition within the Murrindal Limestone (After Wallace, 1982).

The Buchan Group was extensively deformed during the Middle-Late Devonian by the Tabberabberan Orogeny which caused folding, faulting and thrusting of the limestones and mudstones. The underlying volcanics resisted folding and responded to stress by shearing (Jenkin and Baxter, 1968). As a result of this deformation, the north-south trending Buchan Synclinorium was formed, and small blocks of limestone were downfaulted into the volcanics elsewhere in eastern Victoria. Altogether 14 structurally preserved outcrops of the Buchan Group are exposed in the Eastern Highlands with the two largest being at Buchan and Bindi (Talent, 1965).

The Buchan Synclinorium is asymmetrical; the eastern limb dips uniformly at a shallow angle to the west.

However, the western limb dips more steeply; it contains a number of anticlines and synclines and is also cross-cut by two high-angle dip-slip faults with relatively small displacement (<150 m) (Webb et al, in press[1]). The East Buchan Thrust, a shallow dipping reverse fault (45°E), has also affected the southern portion of the eastern limb of the synclinorium.

Late Palaeozoic and Mesozoic sediments are absent in the Buchan area, which probably underwent a period of extended erosion at this time. Early Tertiary (Late Eocene) volcanics occur as discontinuous outcrops to the north and southwest of the study area and are associated with valley filling flows (Wellman, 1974; Webb et al, in press[1]). Middle to Late Tertiary sands and gravels occur mainly in the southern part of the study area and are associated with ancestral or prior river valleys (Webb et al, in press[1]). Recent deposits are limited to stream alluvium and colluvial deposits (Douglas, 1977).

GEOMORPHOLOGY

Three distinct geomorphic units occur within the Eastern Highlands: i) plateau remnants, ii) deeply dissected highlands and iii) intermontane basins (Vandenberg and O'Shea, 1981; L.C.C., 1982). The study area contains the latter two units. A broad open intermontane basin has developed because of the relative ease with which the carbonates of the Buchan Group, particularly the mudstones of the Taravale Formation, are eroded in comparison to the very resistant Snowy River Volcanics. The latter form dissected highlands flanking either side of the Buchan Synclinorium.

Drainage of the area is provided by the southerly flowing Buchan and Murrindal Rivers (Figure 2.6). Upstream of the Buchan Synclinorium, the Buchan River flows through narrow gorges and steep v-shaped valleys cut in Snowy River Volcanics, before it emerges into a broad valley south of Mount Dawson. Within the Buchan Synclinorium the river meanders across the alluvial flats of a 1-2km wide valley cut in the easily erodible mudstones of the Buchan Group. River terraces are present in the valley (Plate 1). Sweeting (1960) recognised three distinct levels, upper terrace, middle or main terrace and lower terrace. Recent work by Webb et al (in press[a]) has shown that the terrace 2m above the present flood plain is the most extensive with only small remnants of the upper river terraces remaining. The Buchan River re-enters the Snowy River Volcanics 6km east of Buchan and continues eastwards for about 3.5km to its confluence with the Snowy River.

The Murrindal River also has its headwaters in non-carbonate rocks, and on reaching the Buchan Group flows southwards approximately along the boundary between the

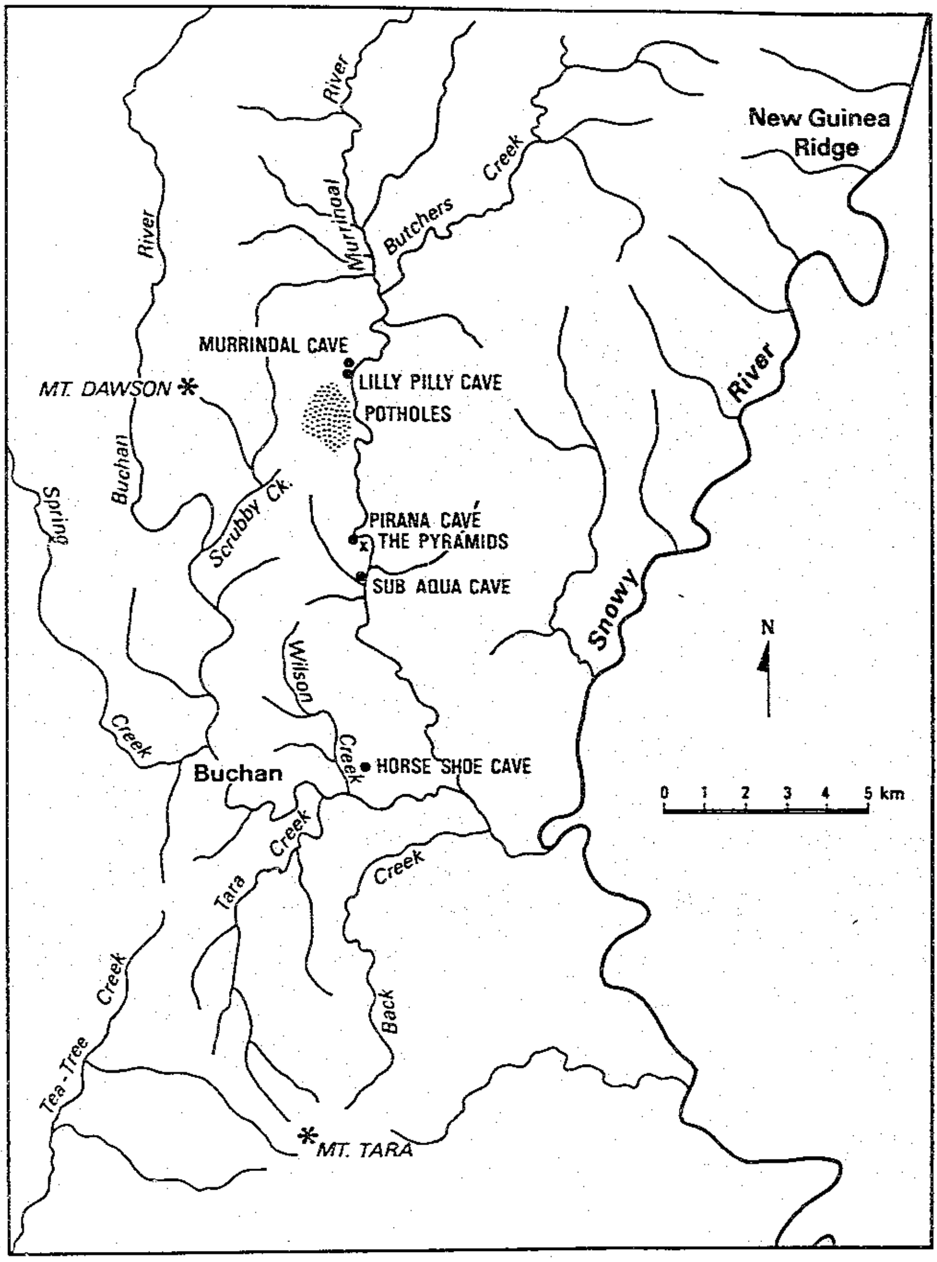

Figure 2.6. Map of the main drainage lines in the study area.

Snowy River Volcanics and Buchan Caves Limestone. There are steep limestone cliffs (up to 80m high, Plate 2) on the western side of the river. Near the Pyramids the Murrindal River disappears underground during periods of low flow into a gravel choked sink (Pirana Cave), and re-appears through the Sub-Aqua cave system some 1.2km

Plate 1. Plate showing the Buchan River valley and terrace development cut into the Taravale Formation 0.5km north of Buchan township.

further south (Plate 3). After turning east and leaving the limestone, the Murrindal River then flows through a rugged tract of Snowy River Volcanics before joining the Buchan River immediately downstream from where that river emerges from the Buchan Group. The valley of the Murrindal River is generally quite narrow though there are some local areas of minor valley widening (just downstream of the Butchers Creek confluence and again near Murrindal and Lilly Pilly caves).

The Buchan River valley has only been widened where it flows across the more easily erodible Taravale Formation; at East Buchan, where it is cut in Buchan

Plate 2. Cliffs cut in Buchan Caves Limestone along the Murrindal River downstream of Sub-Aqua resurgence.

Caves Limestone, the valley is quite narrow with limestone bluffs and cliffs on the southern bank. The Murrindal River flows mainly in Buchan Caves Limestone and has therefore not been able to develop a broad valley.

A number of intermittent streams (e.g. Scrubby Creek and Spring Creek, Figure 2.2) have headwaters on the

Plate 3. Entrance to Sub-Aqua Cave, where under low flow conditions the Murrindal River reappears.

Snowy River Volcanics and sink on reaching the limestone, although after heavy rain they usually persist as surface streams to reach the Buchan River. These intermittent streams form part of the surface network of dry valleys and small blind valleys that have developed on the limestone and are active generally only under high flow conditions (Finlayson and Ellaway, 1987).

Surface stream sinks are all diffuse insurgences (Mylroie, 1984), with flow usually percolating through stream-bed gravels. Surface flow, if any, in many of the blind valley networks (<200m in valley length) is predominantly channelled underground by the simple fact that these valleys terminate in a "doline" or "sink"; the word "doline" is used broadly here in the context of describing a surface depression (which vary considerably in shape and size) into which surface runoff is channelled. Some of these valleys are of the classic blind-valley category, i.e all surface flow is channelled underground (Plate 4); others are of the "semi-blind valley" category, in which on the majority of occasions,

Plate 4. Blind valley in which all surface flow is diverted underground.

when surface flow is evident, all of the flow disappears underground; on rare occasions, depending upon rainfall, antecedent wetness, doline shape and size, etc., the rate at which surface flow arrives at the "doline" is greater than the rate at which it can be channelled underground and surface flow is evident "down valley" from this point (Plate 5). This surface flow does not usually persist as such, for any great distance before it is "captured" by another doline, i.e. they are characteristic of overflow insurgences (Mylroie, 1984).

Finlayson and Ellaway (1987) concluded from an analysis of extreme values of rainfall and runoff that

Plate 5. Semi-blind valley in which under high flow conditions some surface runoff is diverted down valley.

the surface dry valley networks on the Buchan limestones are probably active reasonably frequently, perhaps at intervals of less than eight years on average.

The Horse Shoe Cave - Wilson Creek system (Figure 2.7) is probably the best example in the study area of a blind valley diverting water across a topographic drainage divide into a surface stream system. Blind valleys in the Buchan area usually consist of a sequence of two to four dolines in a valley that divert water underground and it is usually only under high flow conditions that a surface stream will persist to a large doline at the end of the blind valley. The well developed blind valley systems in the study area usually connect to caves.

The best developed and most abundant large scale topographic karst features in the study area are the dolines (Plate 6). The best examples of this landform occur on the Murrindal Limestone in the Potholes area where many dolines can be found; many cave entrances are found in these dolines and more than 90 caves are recorded from this area (McCrae-Williams et al, 1981).

Other large scale exokarst features are uncommon, although where the Buchan Caves Limestone outcrops along the edges of the synclinorium, small areas of bare and covered karren can be found. It is interesting to note

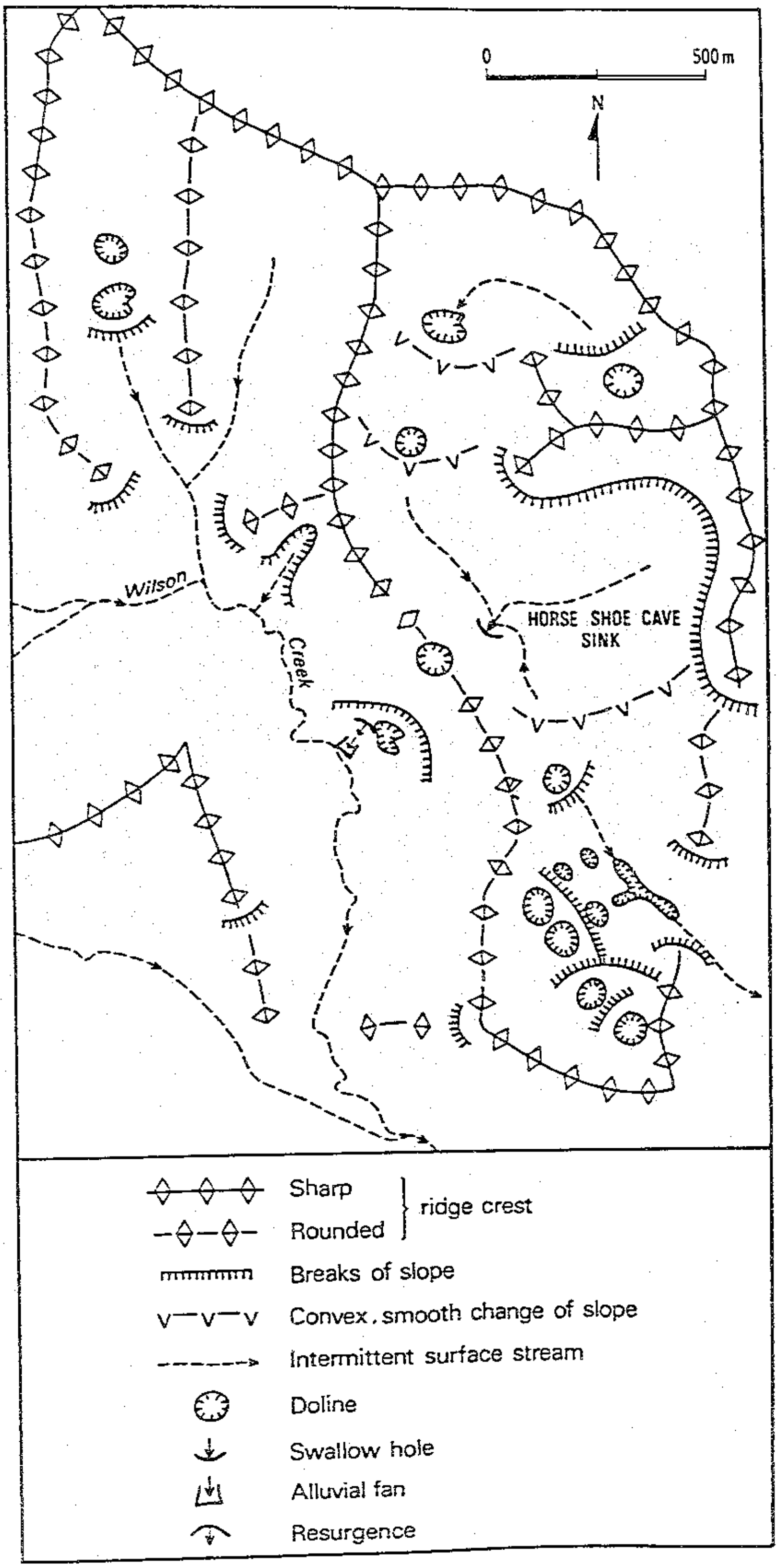

Figure 2.7. Sketch map of Horse Shoe Cave - Wilson Creek system.

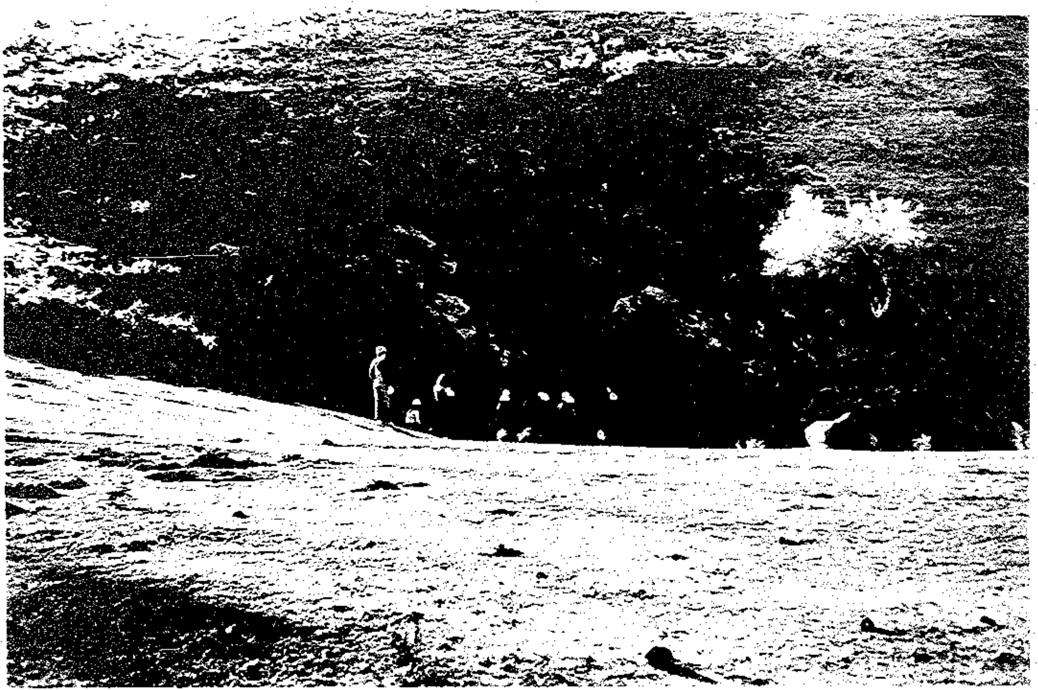

Plate 6. Doline and entrance to Stormwater Tunnel. (Site 19, see Table 3.1 for site description).

the different surface patterns developed beneath a soil cover on the limestone and dolomite sequences of the Buchan Caves Limestone. The limestone surface is usually very smooth and sharp edged along one or more faces whereas the surface developed on dolomite is criss-crossed by quite deep (1-5cms) channels (Plates 7 and 8).

Small-scale surface solutional and other weathering features are relatively common on the limestones with the most widespread forms being rillenkarren (Plate 9) and solutional pans or kamenitza (Plate 10). Solution flutes are generally poorly developed and rarely exceed

Plate 7. Sub-surface weathering features on Buchan Caves Limestone. Note smooth and rounded surfaces.

Plate 8. Sub-surface weathering features on the dolomite sequence of the Buchan Caves Limestone. Note contrast of surface features in Plates 7 and 8.

Plate 9. Small scale solutional flutes (rillenkarren) developed on limestone.

Plate 10. Solutional pan or kamenitza formed in limestone.

Plate 11. Dolomite showing the preferential dissolution of calcite veins due to the different solutional kinetics of calcite and dolomite.

20-30cm in length. Surface solutional features on the dolomite sequence of the Buchan Caves Limestone are limited to a type of "etching" in which the veins of calcite are preferentially dissolved out (Plate 11).

Resurgences, or karst springs, occur only where the Buchan Caves Limestone outcrops along the edges of the synclinorium. These resurgences are located predominantly at, or close to, the base of the limestone or where subsurface drainage lines intersect a change in gradient of a dry surface stream valley. The limestone springs represent the end-point of flow systems ranging from simple diffuse insurgences to more complex flow systems, e.g. the Fairy - Royal - Federal - Dukes cave system (Figure 3.3). Most springs, have both allogenic and autogenic inputs.

Extensive tufa deposits, both modern and old, are evident at two of the spring outlets (Plates 12 and 13), with two other spring sites having much smaller tufa deposits present. The hydrology and chemical characteristics of the water discharging from the karst springs are discussed briefly in Chapter Four, with more detailed discussions being found in Chapters Five, Six and Seven.

The Early Devonian limestones of the Buchan district are one of the largest outcrops of cave and karst forming limestones in southeastern Australia and approximately 300 caverns, sinks and karst related features have been identified by the Australian Speleological Federation (Matthews, 1985).

Caves are relatively common in the Buchan Caves Limestone (on both edges of the synclinorium) and the Murrindal Limestone (northern part of the synclinorium). None of the known caves that occur in the Murrindal Limestone extend into the Buchan Caves Limestone because of the presence of the non-cavernous Pyramids Marlstone between the two limestone units. The caves in the Buchan area can be broadly classified into two main groups:-

Plate 12. Extensive tufa bank developed along the bank of the Buchan River near Bitch of A Ditch (Site 13, see Table 3.1 for site description).

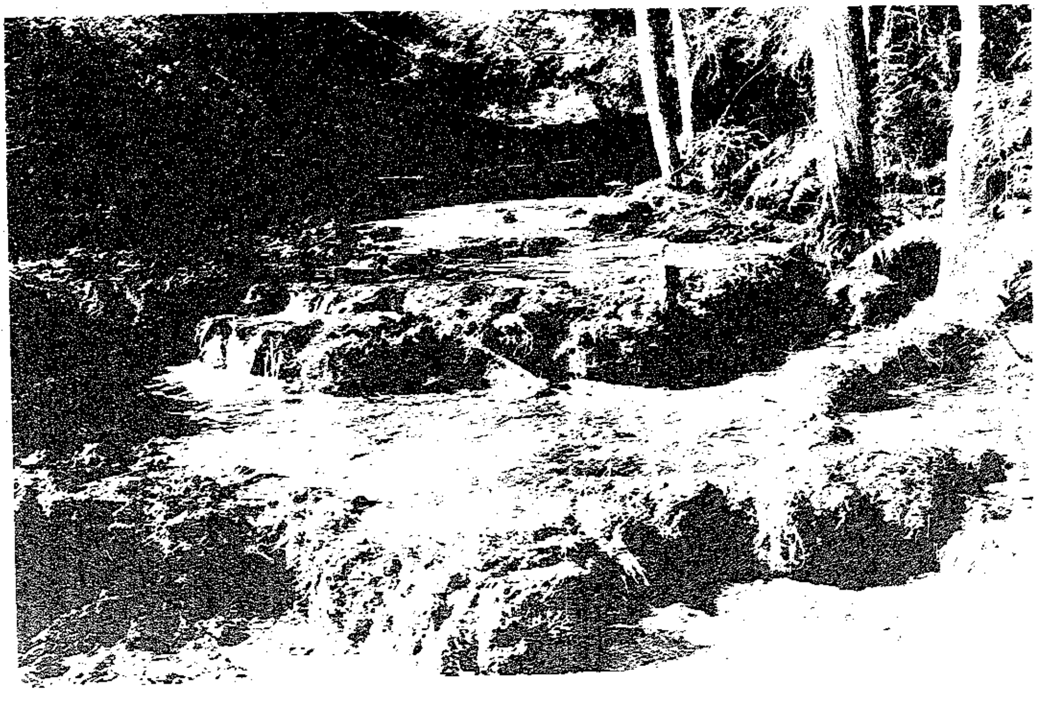

Plate 13. Extensive tufa terraces developed at Scrubby Creek (Site 12b, see Table 3.1 for site description).

i) **Pothole type caves** - these are predominantly vertical caves varying from simple dead-end shafts and rifts to more complex joint-controlled mazes. This cave type can be found throughout the area with the best examples found in the Murrindal Limestone, and,

ii) **Horizontal or stream-passage caves** - these caves occur only in Buchan Caves Limestone and have mostly developed parallel or adjacent to surface valleys and streams. Some have active streams flowing through lower levels, with abandoned upper levels modified by collapse.

CLIMATE AND HYDROLOGY

The Buchan district has a warm temperate climate (Köppen- Geiger classification Cfb) and is subject to the influence of vigorous depressions off the New South Wales coast and incursions of warm, moist subtropical air from the Tasman Sea which together supply the bulk of the rainfall (Linforth, 1969). Rainfall varies considerably with topography, ranging from around 1500mm per annum in the highlands (New Guinea Ridge 800m above sea level (asl)) to 818mm at Buchan with an elevation of 91m asl (Frank and Davey, 1977; L.C.C., 1982). The long term monthly rainfall averages for Buchan (Bureau of Meteorology station no. 084005, over 100 years of record;

Table 2.1) show that on average, rainfall is fairly evenly distributed throughout the year; maximum and minimum monthly rainfall averages are 79mm (October) and 58mm (February) respectively. However, drought and flood conditions are not unusual. The coefficient of variation of annual rainfall is 23.9%.

TABLE 2.1. MEAN MONTHLY AND MEAN ANNUAL RAINFALL DATA (mm) FOR BUCHAN (1883-1989). SOURCE: BUREAU OF METEOROLOGY, MELBOURNE.

STATION NO. 084005, BUCHAN (91.0m a.s.l.)												
JAN.	FEB.	MAR.	APR.	MAY	JUN.	JUL.	AUG.	SEP.	OCT.	NOV.	DEC.	TOTAL
66	58	59	65	67	78	66	60	71	79	74	75	818

No daily air-temperature data are officially recorded at Buchan but mean daily maxima and minima are available for Bairnsdale (station no. 085279, 5m asl; 65kms southwest Buchan) and Orbost (station no.084030, 41m asl; 36kms southeast of Buchan) and are given in Table 2.2. Both stations record mean daily air temperature maxima in February (26.3°C for Bairnsdale and 25.4°C for Orbost) and mean daily minima in July (3.7°C for Bairnsdale and 4.1°C for Orbost). The mean daily minimum and maximum air temperatures for the Buchan area would be relatively similar and most probably lie within 1-2°C of the above figures. Orbost commonly records the maximum daily air-temperature during the winter months for the State of Victoria, and Linforth (1969) attributes this to a Föhn type effect, with northerly winds warming as they descend from the highlands.

TABLE 2.2. MEAN DAILY MINIMUM AND MEAN DAILY MAXIMUM MONTHLY AIR TEMPERATURE DATA (°C), FOR ORBOST AND BAIRNSDALE. SOURCE: BUREAU OF METEOROLOGY, MELBOURNE.

STATION NO. 084030, ORBOST (1938-1989). (41.0 m asl)

	JAN.	FEB.	MAR.	APR.	MAY	JUN.	JUL.	AUG.	SEP.	OCT.	NOV.	DEC.
a)	13.0	13.5	12.1	9.3	6.9	5.1	4.1	4.8	6.2	8.3	10.1	11.7
b)	25.3	25.4	23.8	20.8	17.6	15.0	14.6	15.8	17.7	19.7	21.4	23.6

STATION NO. 085257, BAIRNSDALE COMPOSITE (1970-1989). (5.0 m asl)

	JAN.	FEB.	MAR.	APR.	MAY	JUN.	JUL.	AUG.	SEP.	OCT.	NOV.	DEC.
a)	13.7	14.1	12.3	9.6	6.9	4.8	3.7	4.8	6.4	8.4	10.2	12.0
b)	25.8	26.3	24.1	21.1	18.0	15.0	15.0	16.3	18.3	20.3	21.7	24.3

a = mean daily minimum air temperature
b = mean daily maximum air temperature

Limited air-temperature data from Nowa Nowa (closest meteorological station to Buchan for which reliable data is available) for the periods 1948-1956 and 1965-1975 (station no. 084028, 16m asl; 30kms south of Buchan) show that mean daily maxima (25.8°C for January and February) is reasonably similar to that observed at the two above stations. Mean daily minima of 1.8°C (July) for Nowa Nowa is notably cooler than that observed for either Bairnsdale or Orbost and is probably closer to the value which would be expected at Buchan.

No evaporation data are available from Orbost or Bairnsdale but by using the method of Thornthwaite (modified by Crowe, 1971) potential evapotranspiration can be calculated for both stations. Orbost is closer than Bairnsdale in terms of elevation and mean annual rainfall (41.0m asl and 853mm respectively) to Buchan (91.0m asl and 818mm respectively), so potential evapotranspiration was only calculated from the Orbost data (Table 2.3). Mean monthly rainfall at Orbost exceeds potential evapotranspiration for May, June and July, equals it for August and is less than potential evapotranspiration for the other 8 months of the year giving an overall annual deficit of 342mm. Frost and fog are common in the Buchan valley and mainly occur between April and September. Daily summer air-temperatures of 30°C and over are quite common and can produce effective drought for two to three months.

TABLE 2.3. MEAN MONTHLY RAINFALL DATA (mm) (1883-1985) AND MONTHLY POTENTIAL EVAPOTRANSPIRATION (PE) FOR ORBOST (mm). SOURCE: RAINFALL DATA, BUREAU OF METEOROLOGY, MELBOURNE.

	JAN.	FEB.	MAR.	APR.	MAY	JUN.	JUL.	AUG.	SEP.	OCT.	NOV.	DEC.	TOTAL
MEAN	70	58	69	73	75	85	68	60	70	78	69	78	853
PE.	162	129	129	91	67	45	52	60	82	106	116	156	1195

Mean annual runoff in the Buchan River is 203mm with a coefficient of variation of 65.3% (Table 2.4), (Rural Water Commission, station no. 222206 at Buchan). The Buchan River is also highly variable in terms of flood behaviour with the ratio of the 100 year return period flood to the mean annual flood being 6.9.

Mean annual runoff in the Murrindal River is 149mm with a coefficient of variation of 98.5% (Table 2.4). However as the discharge record for this river dates only from March 1976, and given that the 1974-75 water year discharge for a number of East Gippsland streams is the largest on record (e.g. Timbarra, Buchan and Tambo Rivers) the results obtained must be treated with caution. The Timbarra River, which lies just to the west of the study area (Figure 2.1) and has a similar sized catchment to that of the Murrindal River, has a mean annual runoff of 275mm with a coefficient of variation of 62.8% (using water year data from 1957-1984). Similar values probably apply to the Murrindal River.

TABLE 2.4. RANGE, MEAN AND STANDARD DEVIATION OF DISCHARGE DATA FOR BUCHAN AND MURRINDAL RIVERS (WATER YEARS), ALL VALUES GIGALITRES (10^9 l) EXCEPT n = NUMBER OF WATER YEARS. SOURCE: HYDROGRAPHIC SECTION, RURAL WATER COMMISSION OF VICTORIA.

	BUCHAN RIVER (STATION NO. 222206)	MURRINDAL RIVER (STATION NO. 222216)
range	23.602 - 500.214	2.765 - 124.194
mean	172.482	45.129
s.d.	112.620	44.441
n	37	11

SUMMARY

In this Chapter particular geological, geomorphological and climatological aspects of the study area have been discussed. These three attributes of the study area are considered to be the major determinants influencing the physical and chemical characteristics of the ground and surface waters sampled, which is the major concern of this thesis. The physical and chemical results obtained from the in-situ field measurements and water samples collected from the various sites within the study area are examined and discussed in relationship to the above attributes in Chapters Four, Five and Six.

CHAPTER THREE

METHODS OF ANALYSIS, SAMPLING SITES AND SAMPLING PROGRAM

METHODS OF ANALYSIS

Water temperature, conductivity, pH and Eh values were measured in-situ at each site. A Yellow Springs Instruments model 33M SCT was used for water temperature and conductivity measurements, while a Radiometer PHM 80 digital portable pH meter with the appropriate electrodes was used for pH and Eh measurements. Calibration of the conductivity meter was carried out before each sampling trip in accordance with the manufactures instructions. Calibration of the portable pH meter was carried out in the field after the buffers (pH 4.00 and 7.00) and Zobells solution (Langmuir, 1971b; Eh measurements) were adjusted to the temperature of the water being sampled. Water temperatures were also measured in the field using a calibrated mercury-in-glass thermometer (0-50°C) as a check against the water temperatures measured by the Y.S.I. meter. Air temperature measurements were also made with a calibrated mercury-in-glass thermometer (0-50°C).

Three separate water samples were collected at each site. Two of these samples were filtered in the field (one for cation analysis and the other for chloride and sulphate determinations) using a Sartorius Filter Holder and Whatman GF/C filters (47mm diameter). The filtrate was collected in acid-washed poly-ethylene bottles (6M HNO_3), which were rinsed 3 times at each site before sample collection and then placed on ice. The un-filtered sample (approx. 500 mLs) was collected for alkalinity determination in a pre-rinsed polyethylene bottle and placed on ice. Depending upon which particular chemical analysis was required, e.g. cation analysis, chloride analysis, etc., sample preservation techniques were used in accordance with methods available (Parker, 1972; A.P.H.A., 1976; Stainton et al, 1977; U.S.E.P.A., 1979), e.g. for chloride determinations, water samples were placed on ice and kept below 4.0°C and analysed within seven days of being collected.

Alkalinity was initially determined within six hours of sampling by electrometric titration by titrating against standardised 0.02M HCl to pH 4.5 using an Orion Ion Analyzer and an Orion pH electrode (U.S.E.P.A., 1979). This method was found to be very time consuming and a modification of the alkalinity determination method proposed by Rose (1983) was found to much quicker with very similar results i.e. within ± 2.0%. In the method used the sample is titrated within six hours of sampling against standardised 0.02M HCl (as opposed to standardised 0.1M H_2SO_4) to a pH of 4.5 using BDH 4.5 Indicator Solution.

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Chloride was initially determined using a Corning model 901 Chloride Meter but reproducibility was not good and this method was abandoned in favour of titration against mercuric nitrate (0.0141N) as in Stainton et al (1977).

The filtered water sample collected for cation analysis (Ca^{2+}, Mg^{2+}, Na^+ and K^+) was acidified after collection in the field using a ratio of 0.5 mLs of analytical reagent quality concentrated HNO_3 (nitric acid) per 100 mLs of water sample collected. Calcium and magnesium were determined by atomic absorption spectroscopy using a Varian Model 475 dual beam Atomic Absorption Spectrophotometer. Sodium and potassium were determined by flame photometry using a Corning 410 Flame Photometer with an air-propane mixture. The acidified water samples collected for cation analysis were, before being analysed, subjected firstly to a 1:5 and then either a 1:25 or 1:50 sample dilution (using MilliQ water) depending on ion concentration (using conductivity values as a rough guide to ion concentrations) and all final samples to be analysed, including blanks, were made up to 10,000 ppm lanthanum. Lanthanum is added as a releasing agent (Parker, 1972; U.S.E.P.A., 1979). Calibration standards were prepared from 1000 ppm BDH stock standard solutions for the respective cations, prepared specifically for atomic absorption spectroscopy, with the Ca^{2+} and Mg^{2+} standards also containing 10,000 ppm lanthanum.

Nitrate was determined using an Orion nitrate ion electrode (model no. 93-07) only on the samples collected in October 1982, and as all values were below 0.5 mg/l no further nitrate analyses were carried out. Sulphate was determined gravimetrically (Vogel, 1979) on water samples collected for a number of field-trips (actual number of determinations varied from site to site) but was discontinued because the levels of sulphate determined did not appreciably effect the anion-cation balance of the water samples collected so that the time expended on this analysis could not be justified.

The results obtained from the _in-situ_ field measurements and the chemical analyses were processed using the chemical speciation program, WATSPEC (Wigley, 1977), and water samples were rejected or re-analysed if the ion balance was > ± 4.0%, i.e.,

$$\mathbf{((\Sigma cations - \Sigma anions)/(\Sigma cations + \Sigma anions)) \times 100 > \pm 4.0\%.}$$

(Note cations and anions expressed as milliequivalents). WATSPEC can determine, depending on input data, the level of saturation of the solution with respect to calcite and dolomite (saturation index) and also the theoretical CO_2 partial pressure of a hypothetical coexistent gas phase that is exactly in equilibrium with the analysed water. The saturation index of calcite and dolomite is a means of describing quantitatively the deviation of carbonate waters from equilibrium (White, 1988), and is defined as,

$SI = \log\{IAP/K_{sp}\}$, where IAP and K_{sp} are respectively, the ion activity product for the dissociation of a mineral and the solubility product constant of the same mineral, e.g. for calcite,

$$SI_{cal} = \log(Ca^{2+})_{aq}(CO_3{}^{2-})_{aq}/K_{cal},$$

where a water sample is exactly saturated with calcite when $SI_{cal} = 0$, undersaturated and aggressive when $SI_{cal} < 0.0$, and supersaturated when $SI_{cal} > 0.0$ (as noted in Chapter One).

SAMPLING SITES AND SAMPLING PROGRAM

The remoteness of the study area allowed a limited number of water samples to be collected from a variety of sites over the length of the study period. Water samples were collected at the sites chosen under a variety of hydrological regimes with the two end-members of possible flow conditions being drought (baseflow) and flood (highflow). The number of water samples collected from each site varied considerably depending upon accessibility and flow conditions. Sites sampled included the main surface streams in the area, (all of which have headwaters predominantly on Snowy River Volcanics), intermittent surface streams, karst springs and cave waters and also sites that have been observed to flow only after heavy rain. As the water sampling program progressed, a number of other sites were included. These

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sites were not sampled on a regular basis and were usually only sampled to see if the water at these sites could be linked to other sites e.g. two farm dams and a borehole were sampled on only one occasion to test for high chloride levels found at three cave sites nearby.

As noted above a variety of sites were sampled and these can be divided into groups of similar sites. A brief description of each site sampled is given in Table 3.1 and its location shown in either Figure 3.1 or Figure 3.2.

The main groups of sites are,

1) - major surface streams in the study area,
2) - tributary streams to the Buchan and Murrindal Rivers,
3) - karst spring and cave water sites,

and 4) - miscellaneous sites.

Water samples were collected over a period of nearly six years and include the extremes of drought (February, 1983) and flood (July, 1984). By using rainfall deciles as drought indicators and according to the classification used by Gibbs and Maher (1967), rainfall for 1982 and 1986 is "very much below average", "below average" for 1987, "average" for 1983 and 1984 and "above average" for 1985. Monthly rainfall data over the study period and annual totals are given in Table 3.2 together with mean

TABLE 3.1. SITE DESCRIPTIONS (SEE FIGURES 3.1 AND 3.2 FOR SITE LOCATIONS).

GROUP 1: MAJOR SURFACE STREAMS.

SITE NO.

1) BUCHAN RIVER - Sampling site 300m upstream of bridge over river in township; catchment predominantly on non-carbonate rocks.

2) MURRINDAL RIVER - Sampling site just before river enters main part of Buchan Synclinorium and upstream of Butchers Creek confluence; catchment mainly Snowy River Volcanics and Eocene basalts; may receive input from small outliers of Buchan Caves Limestone.

3) SNOWY RIVER - Major drainage stream in the area which connects to the sea; sampling site upstream of outlier of Buchan Caves Limestone located at New Guinea Ridge; extensive catchment upstream of Buchan River confluence (>10,000 km^2) with predominantly non-carbonate rocks.

GROUP 2: MINOR TRIBUTARY STREAMS.

4) SPRING CREEK - Minor tributary (to the Buchan River) which flows through the Buchan Caves Reserve; usually sinks in gravel bed just below Snowy River Volcanics / Buchan Caves Limestone contact; continuous flow downstream of site 14 input with a small zone of active tufa deposition in bed of stream, also receives input from site 10; water samples collected just upstream of stream sink; catchment predominantly Snowy River Volcanics and small patches of Eocene basalts.

5) BACK CREEK - Intermittent stream with catchment of Snowy River Volcanics and Buchan Caves Limestone; basal part of Buchan Caves Limestone exposed along lower reaches of Back Creek; sampling site just below bridge on Buchan-Orbost road.

6) TARA CREEK - Northerly flowing intermittent stream with catchment mainly Taravale Formation; sampling site just upstream of Buchan River junction.

7) SCRUBBY CREEK 4 - Minor tributary to Buchan River in which flow usually only persists downstream of Scrubby Creek Cave input; upstream of input, stream follows Snowy River Volcanics / Buchan Caves Limestone contact; catchment Snowy River Volcanics, Buchan Caves Limestone and Murrindal Limestone; sampling site 50m downstream of site 12c.

TABLE 3.1(cont.)

GROUP 3: KARST SPRING AND CAVE WATER SITES.

8) NEW GUINEA 2 (NG-2) - Spring located in outlier of Buchan Caves Limestone at New Guinea Ridge; catchment mainly Snowy River Volcanics; important archeological site.

9) NEW GUINEA 6 (NG-6) - Karst window; spring located in large doline in same outlier of Buchan Caves Limestone as sites 8 and 18; assumed to be resurgence of cave stream in Nuigini Namba Faiv cave (NG-5); catchment similar to sites 8 and 18.

10) MOONS (B-54E) - Spring at end of Moons Cave; catchment mainly Snowy River Volcanics and Buchan Caves Limestone.

11) M-4 - Only spring to have been observed to have ceased flowing (February 1983, April and May 1987, and March 1988); catchment mainly Buchan Caves and Murrindal Limestone; possibly receives water draining Snowy River Volcanics.

12a) SCRUBBY CREEK 1 (M-49) - Sampling site inside cave at pool near waterfall, upstream of two large pools covered with calcite rafts.

12b) SCRUBBY CREEK 2 (M-49) - Spring at end of extensive cave system (1600m surveyed passage); catchment similar to site 11; extensive old and new tufa terraces; sampling site where water first emerges.

12c) SCRUBBY CREEK 3 (M-49) - Sampling site at end of extensive series of tufa terraces just before confluence with Scrubby Creek (≈ 65m downstream of site 12b).

13) BITCH OF A DITCH (EB-49) - Spring near contact between Buchan Caves Limestone and Snowy River Volcanics; catchment mainly dolomite sequence of Buchan Caves Limestone; massive relict tufa deposits present.

14) DUKES (B-4) - Spring at end of extensive cave network connecting Fairy, Royal and Federal Caves (3000m surveyed passage); old tufa deposits nearby with active tufa deposition taking place in Spring Creek; outlet extensively modified.

15) SCROOGES VAULT (B-56) - Extensive cave containing deep pools of water usually partially covered with calcite rafts; located in outcrop of Buchan Caves Limestone that contains sites 16 and 17; catchment mainly Taravale Formation but possibly receives water draining from Tertiary sands and gravels.

16) B-67 - Cave containing a small stream that has been linked by dye tracing to the outflow at Dukes (site 14); calcite rafts noticed on some occasions; catchment similar to site 15.

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TABLE 3.1 (cont.)

17) B-41 - Small cave (approx. 8m in length) that ends in a calcite covered pool; catchment similar to sites 15 and 16.

GROUP 4: MISCELLANEOUS SITES.

18) UN-NAMED SEEP - Small seep located in outlier of Buchan Caves Limestone at New Guinea Ridge; evidence of small tufa deposits on Snowy River Volcanics downstream of seep.

19) UN-NAMED CREEK - Surface stream that only flows after heavy rain; water sinks at end of blind valley (Stormwater Tunnel, M-43); assumed to be connected to Scrubby Creek Cave system.

20) BUTCHERS CREEK - Minor tributary of Murrindal River upstream of main limestone body; catchment predominantly Snowy River Volcanics but may receive input from outliers of Buchan Caves Limestone.

21) SUB-AQUA (M-26) - Spring outlet for all of Murrindal River discharge during low flow conditions.

22a) SPRING CREEK (FALLS) - Sampling site just below 10m high waterfall cut into Gelantipy Rhyodacite (member of Snowy River Volcanics); usually only pools of water in gravel stream-bed when sampled; about 1.2km upstream of site 4.

22b) SPRING CREEK UPSTREAM SITE 14 - Small seep in bed of Spring Creek 100m upstream of site 14 input.

22c) SPRING CREEK BETWEEN SITES 14 AND 10 - Sample site in stream channel about 8m upstream of input from site 10.

23) FEDERAL CAVE (B-7) - Sampling site pool of water in lower level just before connecting sump to Dukes Cave.

24) FAIRY CREEK - Intermittent stream observed only to carry flow on rare occasions; joins Spring Creek in Buchan Caves Reserve.

25) WILSONS CAVE (EB-4) - Intermittent outflow cave which was observed to flow only on one occasion; headwaters on Taravale Formation.

26) ROYAL CAVE (B-5) - One of the main tourist caves at Buchan; water sampled from stream observed to flow only on one occasion.

27) SCRUBBY CREEK ABOVE - Pool of water above spring input (site 12b).

TABLE 3.1 (cont.)

28) FARM DAMS - Two farm dams sampled only once; upslope of Buchan Caves Limestone outcrop containing sites 15, 16 and 17; possibly fed by water seeping through Tertiary sands and gravels.

29) UN-NUMBERED BOREHOLE - Un-numbered borehole south of sites 15, 16 and 17; sample taken 0.5m below water surface.

30) TEA-TREE CREEK - Intermittent creek which drains the Tertiary sands and gravels in a southerly direction away from the study area.

31) OVERLAND FLOW - One sample collected of overland flow on Taravale Formation during heavy rain.

32) BELOW BITCH OF A DITCH - Sample site about 10m below large tufa bank.

33) RAINWATER - Rainwater samples collected on three different occasions.

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monthly and mean annual rainfall for Buchan.

Water samples representative of drought conditions were collected in February 1983 when the lowest monthly discharge value in 37 years of continuous gauging record for the Buchan River was recorded (0.059 gigalitres). The 1982-83 water year is the driest on record with a discharge value of 23.6 gigalitres (mean water year discharge value is 172.5 gigalitres and has a coefficient of variation of 65.3%). Using the method of Srikanthan and McMahon (1986) for predicting the recurrence intervals of long hydrologic events, the return periods of the 2, 3 and 4 water year sums ending 1982-83 were 37, 57 and 345 years respectively. The return period of 345 years for the 4 water year sums

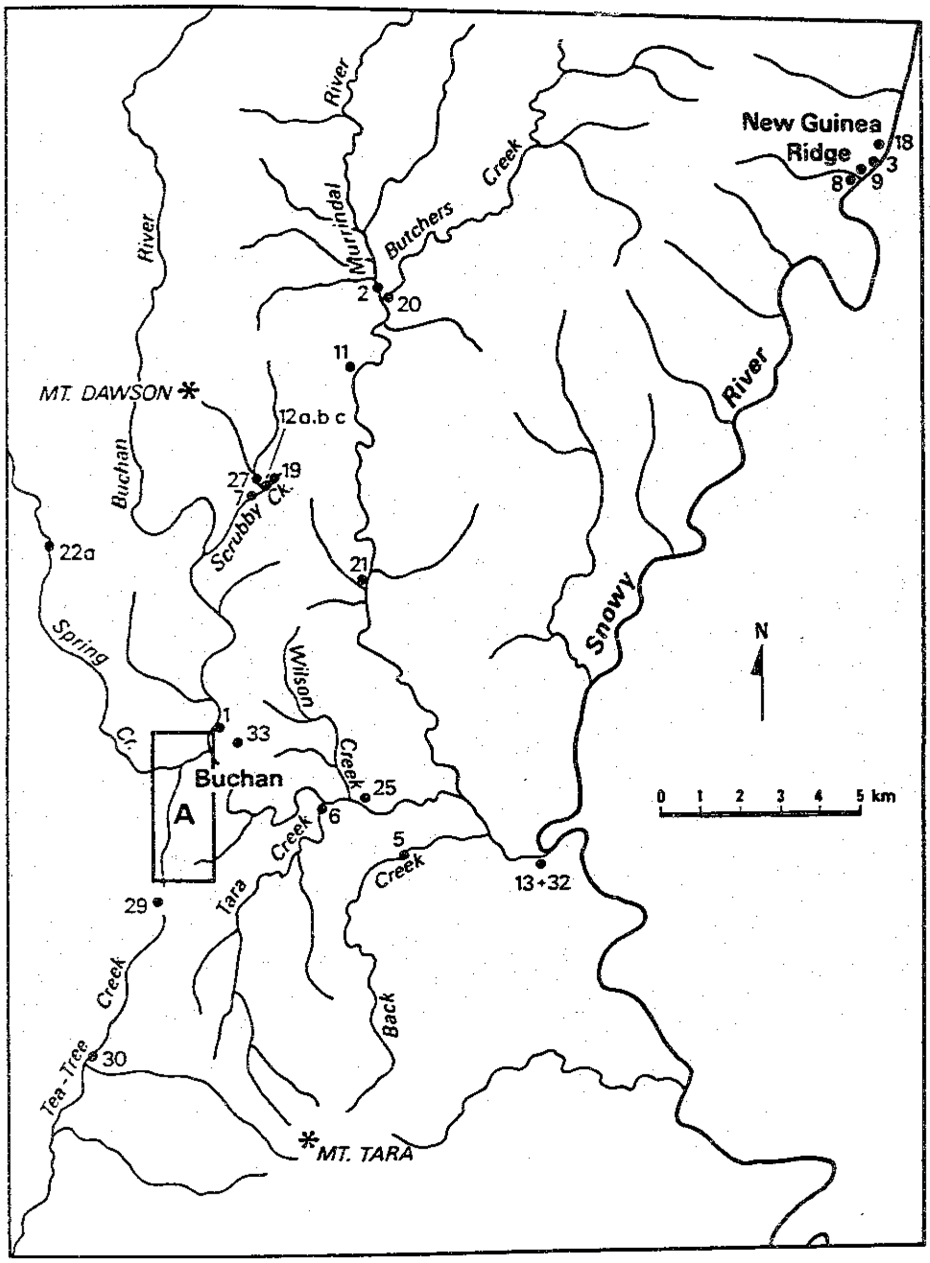

Figure 3.1. Water sample site locations. Sample site numbers as per Table 3.1 (See Figure 3.2 for insert A).

ending 1982-83 is quite significant and represents a period in which most of the southeastern coast of Australia experienced the worst drought on record. Similarly, the Murrindal River also recorded its lowest

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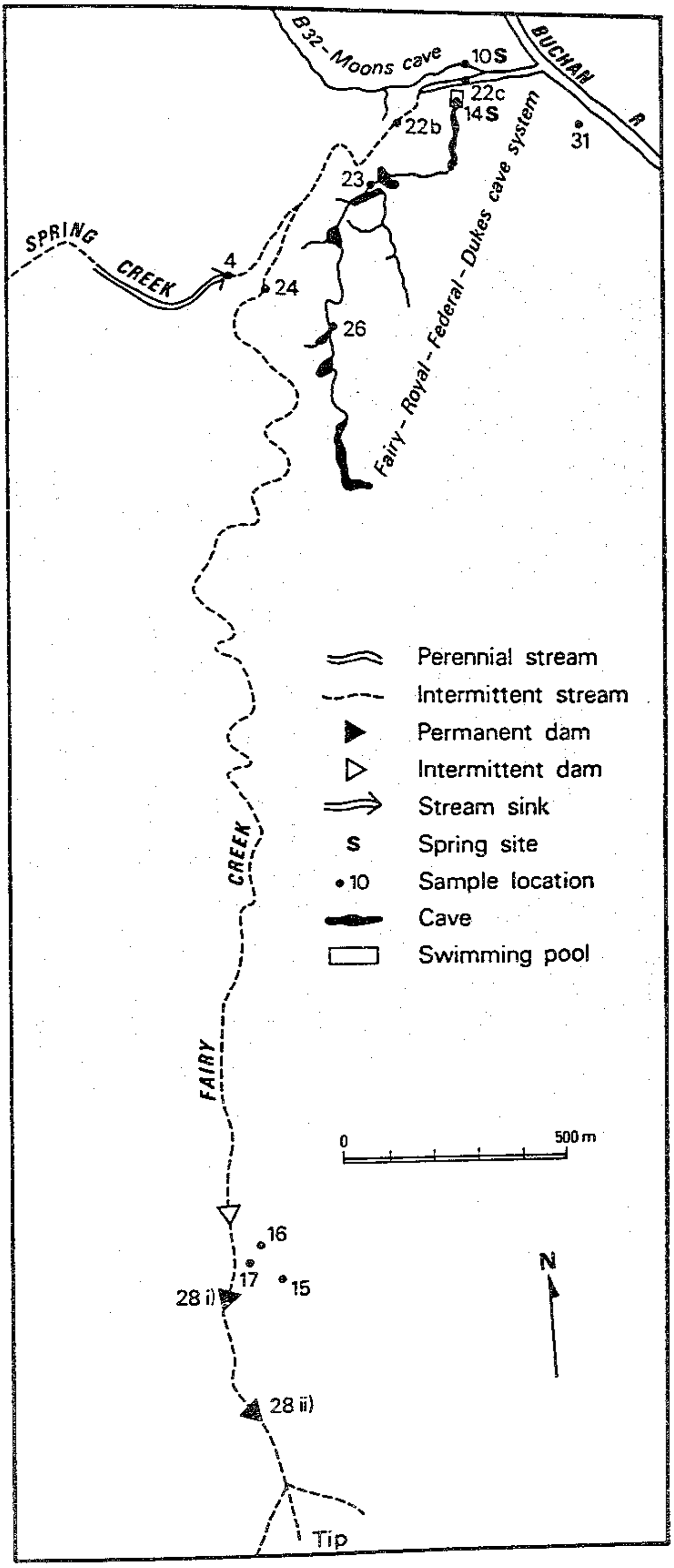

Figure 3.2. Water sample site locations. Sample site numbers as per Table 3.1.

TABLE 3.2. MONTHLY AND YEARLY RAINFALL DATA FOR BUCHAN 1982-1988 (MEAN MONTHLY AND MEAN ANNUAL RAINFALL DATA (mm) USING ALL AVAILABLE DATA. SOURCE: BUREAU OF METEOROLOGY, MELBOURNE.

STATION NO. 084005, BUCHAN (91.0 m a.s.l.).

YEAR	JAN.	FEB.	MAR.	APR.	MAY	JUN.	JUL.	AUG.	SEP.	OCT.	NOV.	DEC.	TOTAL
1982	83	4	119	18	31	48	85	10	55	50	10	52	565
1983	39	15	68	9	147	35	86	73	84	97	40	59	837
1984	99	66	35	38	46	71	217	54	109	28	26	73	862
1985	32	4	57	89	22	98	55	94	146	147	136	20	1084
1986	58	11	17	36	28	25	72	33	63	57	145	30	575
1987	38	76	61	16	60	48	114	52	61	50	50	87	713
1988	61	26	30	82	90	24	14						
mean	66	58	59	65	67	78	66	60	71	79	72	74	815

monthly discharge in February 1983 (0.000, gigalitres). Annual discharge data (in water years) for both the Buchan and Murrindal Rivers commencing the water year 1982-83 is given in Table 3.3.

The highest monthly mean daily air temperature on record for both Orbost and Bairnsdale was recorded in February 1983 (29.3°C and 29.1°C respectively). At the time the water samples were collected, February 1983, both the Buchan and Murrindal Rivers had ceased to flow and consisted only of pools of water. All but one of the karst springs continued to flow (Ellaway and Finlayson, 1984).

Water samples representing high flow (flood)

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TABLE 3.3. ANNUAL DISCHARGE DATA (WATER YEARS) FOR THE BUCHAN AND MURRINDAL RIVERS COMMENCING WATER YEAR 1982-83 (GIGALITRES). MEAN ANNUAL DISCHARGE, STANDARD DEVIATION AND CO-EFFICIENT OF VARIATION USING ALL AVAILABLE DATA. SOURCE: HYDROGRAPHIC SECTION, RURAL WATER COMMISSION OF VICTORIA.

	BUCHAN RIVER (Station no. 222206) (1948-1987)	MURRINDAL RIVER (Station no. 222216) (1976-1987)
1982-83	23.602	3.950
1983-84	176.285	54.860
1984-85	162.915	64.817
1985-86	282.740	124.194
1986-87	80.441	10.472
mean	172.482	45.129
s.d. (c.v.)	112.620 (65.3%)	44.441 (98.5%)

conditions were collected in July 1984 when over 110mm of rain fell in a 48 hour period (28th and 29th) onto an already wet catchment causing severe flooding of the main surface streams in the area. Rainfall for July 1984 up to the 28th was 107mm (41mm over the long term mean for July). Dry valley networks were suddenly activated and caves in the area that had previously been assumed to be abandoned were observed to be carrying large volumes of highly turbid water. The tourist caves in the Buchan Caves Reserve were closed due to severe flooding. The instantaneous maximum flow of 19.3 gigalitres/day was the fifth highest on record for the Buchan River and the highest recorded during the study period. Maximum instantaneous flow of the Murrindal River at the gauge site in East Buchan was 32.7 gigalitres/day, the highest on record although records are only available from March, 1976. Recurrence analysis of the flood event, using both rainfall intensity (mm per day) and discharge data for the Buchan River (mean daily flow) by Finlayson and Ellaway (1987) gave an average recurrence interval of between four and eight years.

SUMMARY

In this Chapter the variety of sites from which water samples were collected and the methods of analysis used to determine particular parameter values are described. Hydrological and climatological conditions operating in the study area over the study period are also briefly described. Karst spring water samples that are assumed to represent the two end-members of possible flow regimes, i.e. baseflow (drought conditions) and high flow (flood conditions) were collected in February 1983 and July 1984 respectively. The effect of these two events on the long term chemical behaviour and flow characteristic of the karst spring sites sampled is briefly discussed in Chapter Four and examined in more detail in Chapter Six.

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CHAPTER FOUR

CLASSIFICATION OF WATER TYPES

INTRODUCTION

In this Chapter the results obtained from the field and laboratory work are presented in three sections:- i) *in-situ* field measurements, ii) chemical parameters, and iii) computed parameters, with each of these sections being subdivided into the categories of sites sampled. In Chapter Three it was noted that the sites sampled were divided into four groups; in this Chapter the major surface and minor tributary stream sites will discussed as one group and not as two separate groups for the discussions on the results obtained for the *in-situ* field measurements and the computed parameters.

Based on results and trends found for each section the sites sampled are subjectively classified into sites having water of particular physical and chemical characteristics. A cluster analysis technique is then used for comparison.

Assuming the data obtained for each parameter at each site are normally distributed the arithmetic mean and the standard deviation (S.D.) would be the best measures of central tendency and dispersion respectively. Statistical analysis of the data obtained at each site shows that some parameters are not normally distributed as indicated by high positive or negative skew. For these parameters the median value (Q_{50}) and the semi inter-quartile range (SIQ) provide the best measures of central tendency and dispersion.

Since it is inappropriate to include the mean for some parameters and the median for others, the mean and the median together with the standard deviation (S.D.) and the semi inter-quartile range (S.I.Q.), are presented for most variables in the tables found in this Chapter. Skewness, a measure of the degree of asymmetry in distribution is also given.

To facilitate discussion, comparisons between sites are based on median values only. It is felt that the median is more representative of the samples collected, being little affected by particularly low and high values which can make the arithmetic mean completely unrepresentative (King, 1969; Chase, 1976). Also where data are approximately normal the median and the mean are quite similar in value.

IN-SITU FIELD MEASUREMENTS

The range, median, SIQ, mean, S.D. and skewness for water temperature (°C), Eh (millivolts, mV), pH and conductivity (μS cm^{-1}, 25.0°C) are given in Tables 4.1, 4.2 and 4.3 for the groups of sites sampled (see Table 3.1), i.e. the major surface streams, the minor tributary streams, the karst spring and cave waters and the miscellaneous sites respectively. Also presented in Table 4.1 are the range, median, S.I.Q., mean, S.D. and skewness for available monthly water temperature, pH and conductivity data measured by the Rural Water Commission (R.W.C.) for the Buchan River (1975-1989) at Buchan and the Snowy River at Jarrahmond (1975-1989).

MAJOR SURFACE AND MINOR TRIBUTARY STREAM SITES

WATER TEMPERATURE

Median water temperatures found in this study ranged from 13.0°C at Spring Creek (site 4) to 18.5°C at the Snowy River (site 3) with the Murrindal River (site 2) and Scrubby Creek 4 (site 7) having the greatest (25.0°C) and smallest (5.5°C) ranges respectively (Table 4.1). Of the four sites sampled in February 1983 (Buchan River (site 1), Murrindal River, Snowy River and Spring Creek) all recorded the highest water temperature measured over the study period, although in the case of the Buchan River this water temperature value was recorded on one other occasion.

It is interesting to note that the warmest water temperature recorded for the Buchan and Snowy Rivers over the study period, using the R.W.C. data, were also recorded in February 1983 (25.0°C and 29.5°C respectively). These maximum water temperature values were noted to occur on only three other occasions for the Buchan River and on only one other occasion for the Snowy River using all R.W.C data and this is an indication of how extreme conditions were in the study area in February 1983.

Of the five sites sampled during the high flow event in July 1984 (Buchan River, Murrindal River, Snowy River, Spring Creek and Back Creek (site 5)), four of the sites had water temperatures very similar to one another (9.0-10.0°C) with the Snowy River site recording 12.0°C. Back Creek was the only site sampled in this group for which it was the minimum value recorded.

Median water temperatures for the Buchan and Snowy Rivers (using the R.W.C. data) are quite similar, with

TABLE 4.1. RESULTS OF IN-SITU MEASUREMENTS OF WATER TEMPERATURE (°C), Eh (mV), pH AND CONDUCTIVITY (μS cm^{-1} 25°C) FOR MAJOR AND MINOR TRIBUTARY STREAMS (SITE NUMBERS AS IN TABLE 3.1). RANGE, MEDIAN, SEMI INTER-QUARTILE RANGE (S.I.Q.), MEAN, STANDARD DEVIATION (S.D.) AND SKEWNESS VALUES GIVEN (n = NUMBER OF SAMPLES). DATA FOR BUCHAN (##) AND SNOWY (**) RIVERS FROM RURAL WATER COMMISSION.

SITE NO.		WATER TEMPERATURE (°C)	Eh (mV)	pH	CONDUCTIVITY (μS cm^{-1} 25°C)
MAJOR SURFACE STREAMS					
1)	range	7.0 - 21.5	391 - 504	6.86 - 8.16	54 - 600
	median	14.5	420	7.53	99
	S.I.Q.	4.4	16	0.19	48
	mean	14.9	423	7.56	156
	S.D.	4.7	29	0.33	146
	skewness	-0.09	1.33	0.10	2.13
	n =	(20)	(16)	(20)	(18)
2)	range	6.0 - 31.0	361 - 440	7.02 - 8.18	224 - 522
	median	17.0	416	7.51	271
	S.I.Q.	4.4	15	0.15	28
	mean	16.4	413	7.51	301
	S.D.	6.3	22	0.30	79
	skewness	0.45	-0.95	0.39	1.59
	n =	(19)	(12)	(19)	(18)
3)	range	11.0 - 24.0	386 - 459	7.38 - 8.53	135 - 245
	median	18.5	400	7.83	185
	S.I.Q.	4.3	11	0.31	30
	mean	17.8	410	7.84	183
	S.D.	5.0	25	0.36	79
	skewness	-0.11	1.21	0.44	0.12
	n =	(10)	(8)	(10)	(9)
##	range	1.0 - 25.0	-	6.30 - 8.30	32 - 880
	median	14.8	-	7.55	87
	S.I.Q.	5.5	-	0.30	27
	mean	14.2	-	7.47	106
	S.D.	6.1	-	0.40	89
	skewness	-0.08	-	-0.61	6.38
	n =	(152)	-	(112)	(174)
**	range	3.0 - 29.5	-	6.50 - 8.60	62 - 240
	median	15.0	-	7.80	148
	S.I.Q.	5.7	-	0.35	23
	mean	15.6	-	7.75	151
	S.D.	6.6	-	0.45	36
	skewness	-0.10	-	-0.49	0.27
	n =	(107)	-	(97)	(173)
MINOR TRIBUTARY STREAMS					
4)	range	7.0 - 19.0	301 - 457	6.82 - 7.80	149 - 1015
	median	13.0	418	7.38	355
	S.I.Q.	2.6	14	0.39	107
	mean	12.4	408	7.33	436
	S.D.	3.2	40	0.27	233
	skewness	-0.08	-1.57	-0.05	1.03
	n =	(23)	(16)	(23)	(22)
5)	range	9.9 - 18.0	187 - 435	6.81 - 7.86	264 - 984
	median	15.5	386	7.49	781
	S.I.Q.	3.0	35	0.16	58
	mean	14.1	367	7.39	723
	S.D.	3.2	80	0.33	206
	skewness	-0.27	-1.52	-0.61	-1.13
	n =	(10)	(9)	(10)	(9)
6)	range	9.0 - 22.0	344 - 433	7.32 - 7.88	612 - 790
	median	18.0	407	7.63	696
	S.I.Q.	2.9	24	0.14	46
	mean	16.5	398	7.62	676
	skewness	-0.51	-0.64	-0.46	0.41
	S.D.	3.9	36	0.18	58
	n =	(11)	(7)	(11)	(11)

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TABLE 4.1 (cont.)

7)	range	13.5 - 19.0	391 - 432	7.80 - 8.32	455 - 610
	median	15.0	419	8.02	552
	S.I.Q.	1.5	11	0.09	36
	mean	15.5	415	8.01	546
	S.D.	1.7	15	0.14	51
	skewness	0.60	-0.65	0.39	-0.62
	n =	(13)	(8)	(13)	(13)

the median values obtained in this study for the Buchan River, Back Creek and Scrubby Creek 4 also being reasonably similar.

The minor tributary stream sites record smaller S.I.Q.'s than the major surface streams. This perhaps is a reflection of the fact that the four minor surface streams are, for most of the time, fed by seepage and ground waters rather than surface runoff and hence do not respond as readily or as easily as the major surface stream sites do due to seasonal effects. This is particularly the case for Scrubby Creek 4 whose flow is predominantly derived from the Scrubby Creek cave system. This "seasonality" factor is discussed in more detail in Chapter Six.

Eh

The median Eh's are reasonably similar for all sites with the minor tributary stream sites, except Scrubby Creek 4, tending to have the greater range (Table 4.1). Median Eh's obtained in this study are plotted together with median pH's for the respective sites on an Eh/pH diagram (Figure 4.1) and are noted to lie within the

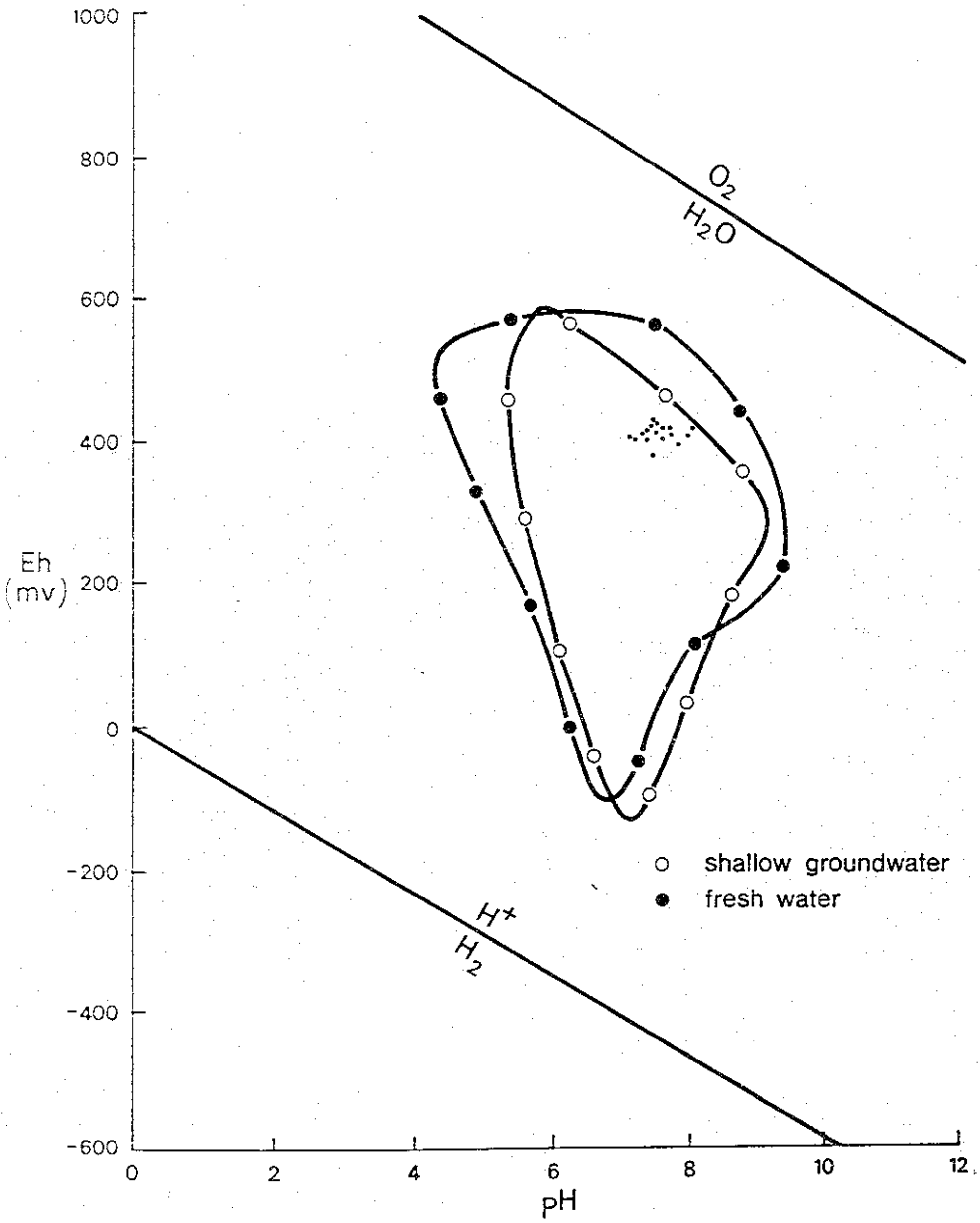

Figure 4.1. Eh/pH diagram with median Eh and pH values plotted for surface stream and karst spring and cave water sites (·). Shallow groundwater and fresh water boundaries after Bass Becking et al, 1960.

approximate "boundaries" of Eh and pH values for shallow groundwater and fresh water environments assembled by Bass Becking et al (1960). Also the median data for the karst spring and cave water sites is given in Figure 4.1. All sites are tightly clustered together and indicate

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similar oxidising environments.

It must be stressed that the Eh measurements made in this study were taken simply to distinguish between oxidising and reducing environments and not as electrochemical data for thermodynamic interpretation. In broad terms, lower Eh's were noted to occur when stream discharges were low; this was particularly noticeable for three of the minor tributary streams (Spring Creek, Back Creek and Tara Creek) more so than for the other sites sampled.

pH

Median pH for the major surface stream sites were within the range of median values noted for the minor streams, although the major surface stream sites generally exhibited the greater range of values found (Table 4.1). Of the five sites sampled during the high flow event (July, 1984) the four sites that recorded similar water temperatures also recorded quite similar pH values (7.27-7.38). For these four sites the similar water temperature and pH values could indicate the same source of water. That is, it possibly indicates runoff passing through the system so quickly that there is little chance of any chemical reactions taking place. This is examined in more detail in the chemical results section.

CONDUCTIVITY

Unfortunately no conductivity measurements were obtained for any of the sites sampled in July 1984, but an approximation of conductivity can be obtained by multiplying the concentration of each ion determined by the appropriate conductivity factor and summing (A.P.H.A., 1976). For the sites sampled in July 1984 the calculated conductivity value is the lowest for all sites except the Buchan River.

Median conductivity varied considerably between the sites and within the two surface stream groups (Table 4.1). Spring Creek had the greatest range and largest S.I.Q. of both groups although its median was intermediate between the medians obtained for the major surface streams and the other three minor tributary streams. Broadly, three different types of waters can be seen to exist if median conductivities are used to distinguish between the sites: - A): 99-185 μS cm^{-1} (Buchan and Snowy Rivers); - B): 271-355 μS cm^{-1} (Murrindal River and Spring Creek); and - C): 552-781 μS cm^{-1} (Scrubby Creek 4, Tara Creek and Back Creek).

The range in median conductivities for these sites varied considerably (99-781 μS cm^{-1}) and as conductivity is an indirect measure of the concentration of ions in solution, conductivity is perhaps simply reflecting the effect of catchment lithology on water chemistry. For example, the Buchan and Snowy Rivers which have > 99% of their respective catchments on less soluble non-carbonate lithologies have relative low median conductivity values when compared to minor tributary streams such as Back and Tara Creeks which drain catchments composed of predominantly carbonate material. This effect of catchment lithology on water chemistry and chemical ion concentrations is examined in more detail in Chapter Five and Six.

The highest conductivity reading observed for the Buchan and Murrindal Rivers over the study period (600 and 522 μS cm^{-1} respectively), were recorded in February 1983. The highest conductivity readings recorded for the Buchan River using the R.W.C. data were in February and March 1983 respectively (770 and 880 μS cm^{-1}). For Spring Creek the second highest value recorded (851 μS cm^{-1}) was in February 1983.

Comparing the results found in this study for water temperature, pH and conductivity measurements for the Buchan and Snowy Rivers with the data available from the R.W.C. for these two rivers, the values measured in this study tended to lie within the range of values found by the R.W.C. for all parameters. Median pH, water temperature and conductivity values for the Buchan River were relatively similar for both data sets. For the Snowy River, only median pH was similar to the R.W.C. data

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with the median water temperature and conductivity values found in this study being considerably higher than the corresponding medians using the R.W.C. data. The small number of <u>in-situ</u> field measurements made in this study for this site, particularly with more measurements occurring during the warmer months could help explain some of the discrepancy, the other being the time period over which the data from the R.W.C. were assembled.

KARST SPRING AND CAVE WATER SITES

WATER TEMPERATURE

The range of median water temperatures noted for this group of sites (Table 4.2) lie within the range of median water temperatures noted for the major and minor surface streams. Medians for this group ranged from 13.5°C (New Guinea 6 - site 9) to 17.0°C (Bitch of a Ditch and B-67 - sites 13 and 16 respectively). In comparing the data for this group of sites with that obtained for the major and minor surface streams the considerably smaller S.I.Q.'s associated with the karst spring and cave water sites are quite noticeable as is the range of values noted at any of these sites. This is the result of the damping effect of storage delays in the karst aquifer. This issue is discussed in more detail in Chapter Six.

Of the nine sites in this group that were sampled in

TABLE 4.2. RESULTS OF IN-SITU MEASUREMENTS OF WATER TEMPERATURE (°C), Eh (mV), pH AND CONDUCTIVITY ($\mu S\ cm^{-1}$ 25°C) FOR KARST SPRING AND CAVE WATER SITES. (SITE NUMBERS AS IN TABLE 3.1). RANGE, MEDIAN, SEMI INTER-QUARTILE RANGE (S.I.Q.), MEAN, STANDARD DEVIATION (S.D.) AND SKEWNESS VALUES GIVEN (n = NUMBER OF SAMPLES).

SITE NO.		WATER TEMPERATURE (°C)	Eh (mV)	pH	CONDUCTIVITY ($\mu S\ cm^{-1}$ 25°C)
8)	range	12.0 - 16.8	386 - 448	7.09 - 7.93	210 - 514
	median	14.0	413	7.38	246
	S.I.Q.	0.9	6	0.35	77
	mean	14.2	416	7.44	297
	S.D.	1.6	19	0.33	118
	skewness	0.51	0.21	0.33	0.80
	n =	(8)	(7)	(8)	(8)
9)	range	12.0 - 15.0	414 - 452	6.68 - 8.00	160 - 517
	median	13.5	426	7.44	268
	S.I.Q.	0.5	9	0.24	70
	mean	13.5	432	7.37	294
	S.D.	0.9	14	0.40	116
	skewness	0.0	0.25	-0.23	0.84
	n =	(8)	(7)	(8)	(8)
10)	range	12.0 - 16.0	357 - 463	6.87 - 7.96	208 - 668
	median	13.5	425	7.41	567
	S.I.Q.	0.5	10	0.11	158
	mean	13.6	423	7.45	496
	S.D.	0.9	23	0.24	161
	skewness	0.86	-1.23	-0.03	-0.62
	n =	(29)	(15)	(29)	(28)
11)	range	10.5 - 17.0	391 - 430	7.10 - 8.21	389 - 890
	median	15.0	416	7.65	690
	S.I.Q.	0.4	12	0.26	73
	mean	14.6	414	7.68	661
	S.D.	1.5	13	0.34	146
	skewness	-1.33	-0.31	-0.14	-0.45
	n =	(18)	(12)	(18)	(17)
12a)	range	14.0 - 17.0	381 - 423	7.12 - 7.94	325 - 732
	median	16.0	414	7.49	610
	S.I.Q.	0.6	9	0.22	74
	mean	15.8	409	7.52	594
	S.D.	1.1	13	0.28	125
	skewness	-0.82	-0.92	0.08	-0.97
	n =	(12)	(10)	(12)	(12)
12b)	range	11.5 - 17.0	373 - 427	7.05 - 8.01	330 - 713
	median	16.0	411	7.64	611
	S.I.Q.	0.8	8	0.10	57
	mean	15.7	410	7.58	594
	S.D.	1.2	13	0.27	102
	skewness	-1.98	-1.29	-0.96	-1.30
	n =	(22)	(15)	(22)	(19)
12c)	range	11.5 - 19.0	373 - 427	7.10 - 8.23	319 - 633
	median	16.0	415	7.94	543
	S.I.Q.	0.8	9	0.14	44
	mean	15.9	411	7.83	532
	S.D.	1.8	15	0.34	80
	skewness	-0.13	-1.12	-1.07	-1.06
	n =	(21)	(14)	(21)	(20)
13)	range	16.0 - 18.0	375 - 445	7.00 - 7.96	710 - 1080
	median	17.0	415	7.48	958
	S.I.Q.	0.3	5	0.16	18
	mean	16.9	414	7.44	952
	S.D.	0.4	17	0.25	85
	skewness	0.25	-0.57	0.24	-1.16
	n =	(20)	(16)	(20)	(17)

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TABLE 4.2 (cont.).

14)	range	13.0 - 18.0	380 - 483	6.62 - 7.45	540 - 1616
	median	16.9	416	7.12	1364
	S.I.Q.	0.3	12	0.14	46
	mean	16.6	417	7.09	1303
	S.D.	0.9	23	0.20	260
	skewness	-2.12	1.18	-0.29	-1.94
	n =	(31)	(18)	(30)	(30)
15)	range	15.0 - 17.0	400 - 441	7.11 - 7.51	840 - 1159
	median	16.5	410	7.31	1064
	S.I.Q.	0.3	9	0.09	50
	mean	16.5	415	7.31	1043
	S.D.	0.7	15	0.15	106
	skewness	-1.53	0.91	0.25	-0.97
	n =	(7)	(6)	(7)	(7)
16)	range	12.0 - 19.0	337 - 430	6.77 - 7.39	1122 - 1824
	median	17.0	414	7.06	1691
	S.I.Q.	0.5	22	0.08	45
	mean	16.6	401	7.05	1654
	S.D.	1.2	30	0.14	144
	skewness	-2.15	-0.92	0.31	-2.46
	n =	(22)	(15)	(22)	(21)
17)	range	14.7 - 17.5	401 - 439	6.89 - 7.21	1281 - 1809
	median	16.5	416	7.09	1602
	S.I.Q.	0.3	10	0.07	10
	mean	16.3	418	7.05	1603
	S.D.	0.8	13	0.10	121
	skewness	-0.86	0.25	-0.08	-1.16
	n =	(13)	(8)	(13)	(13)

February 1983 (New Guinea 2 (site 8), New Guinea 6, Moons (site 10), Scrubby Creek 1, 2 and 3 (sites 12a, 12b and 12c respectively), Bitch of a Ditch, Dukes (site 14) and B-67) all except Bitch of a Ditch recorded highest water temperature over the study period on this occasion or in the case of Moons, Scrubby Creek 1 and Dukes on one other occasion.

Also on this occasion the range of water temperatures recorded for this group of sites, 15.0°C (New Guinea 6) to 19.5°C (Scrubby Creek 3) is considerably smaller, and the individual sites were generally cooler than the range and individual values noted for the major and minor tributary streams on this occasion (19.0°C - Spring Creek to 31.0°C Murrindal River).

Of the seven sites sampled during the high flow event in July 1984 (Moons, M-4, Scrubby Creek 2 and 3, Bitch of a Ditch, Dukes and B-67) all except Moons recorded the lowest water temperatures noted over the study period. Bitch of a Ditch showed the least amount of change; only 1.0°C lower than the median. The other sites recorded values in the range 11.5°C to 13.0°C which are marginally warmer than the 9.0-10.0°C noted for three of the major and minor surface stream sites sampled on this occasion.

The karst spring and cave water sites sampled can be divided into three groups with similar median water temperatures: Group 1, 13.5-14.0°C (3 sites); Group 2, 15.0-16.0°C (4 sites); and Group 3, 16.5-17.0°C (5 sites). This grouping of the karst spring and cave water sites is discussed in more detail in other sections of this Chapter.

Eh

Median Eh values for these sites are relatively similar and together with the relevant median pH are shown in Figure 4.1 together with the median Eh/pH values for the major surface and minor tributary streams. They show that these waters are all well oxidised.

pH

Median pH values ranged from 7.06 (B-67) to 7.94 (Scrubby Creek 3) which is reasonably similar to the range of values noted for the major and minor surface streams.

For the high flow event in July 1984, five of the seven sites sampled (M-4, Scrubby Creek 2, Scrubby Creek 3, Bitch of a Ditch and B-67) had pH values in the range 7.04-7.11 with the two other sites having pH values of 7.38 (Moons) and 7.43 (Dukes).

In Chapter One it was noted that degassing of karst spring water as it flows downstream from the spring outlet is a major control on pH values, i.e pH was shown to increase as degassing continued. This is most evident at the Scrubby Creek sites where median pH increases from 7.49 (Scrubby Creek 1 - cave water) to 7.64 (Scrubby Creek 2 - spring outlet) to 7.94 (Scrubby Creek 3, ≈65m downstream) to 8.02 (Scrubby Creek 4, a further 50m downstream). This degassing effect is discussed in more detail in Chapter Seven.

CONDUCTIVITY

Median conductivity values varied considerably from site to site and ranged from 246 $\mu S\ cm^{-1}$ (New Guinea 2) to 1691 $\mu S\ cm^{-1}$ (B-67) with B-41 and Moons having the smallest and largest S.I.Q.'s respectively.

As noted previously for the major surface and minor tributary streams, no conductivity values are available for any site sampled in July 1984. For most sites conductivity measurements made in September 1984 were the lowest recorded over the study period. Calculated conductivity values for the July 1984 water samples are notably lower than the September conductivity values for all sites except Dukes. Whether the conductivity measurements made in September 1984 were still being influenced by the July high flow event is a matter of conjecture and will be looked at in Chapter Six.

Karst Spring and Cave Water Types:

Using the medians obtained for water temperature, pH and conductivity the karst spring and cave water sites can be divided into sites exhibiting four different types of water. The three Scrubby Creek sites are grouped together as they in fact represent the same body of ground water; differences noted in median conductivity and pH values for these three sites are attributed simply to degassing and calcite precipitation (see Chapter Seven) and unless otherwise noted only Scrubby Creek 2 data will be used.

TYPE 1 – New Guinea 2 and New Guinea 6: low median conductivities (246-268 $\mu S\ cm^{-1}$) which are closer to the median values obtained for the Murrindal River (271 $\mu S\ cm^{-1}$) and Spring Creek (355 $\mu S\ cm^{-1}$) than for those obtained for the other karst spring and cave water sites. Water temperatures are usually the coolest of the karst spring and cave water sites, with the exception of Moons, and are similar to the median for Spring Creek. Median pH's are similar to that observed for Spring Creek and Moons.

TYPE 2 - M-4 and Scrubby Creek 2: median conductivity values (611-690 μS cm-1) lie within the median range noted for three of the minor tributary streams (Back Creek, Tara Creek and Scrubby Creek 4); median pH values (7.62-7.64) similar to that for Tara Creek (7.63); median water temperature (15.0-16.0°C) similar to that noted for Back Creek and Scrubby Creek 4.

TYPE 3 - Bitch of a Ditch and Scrooges Vault (site 15): median water temperature, pH and conductivity values of 16.5-17.0°C, 7.31-7.48 and 958-1064 μS cm^{-1} respectively.

TYPE 4 - B-67 and B-41 (site 17): highest median conductivity values of all sites sampled (1602-1691 μS cm^{-1} respectively); lowest median pH (7.06-7.09); median water temperatures similar to that observed for TYPE 3 waters (16.5-17.0°C).

Median <u>in-situ</u> values for Moons and Dukes, in particular the conductivity's (567 and 1364 μS cm^{-1}

respectively), lie between those values observed for water TYPES 1 and 2 and water TYPES 3 and 4 respectively. Moons is closer in terms of conductivity to TYPE 2 water although median water temperature and pH are similar to the medians for these two parameters for TYPE 1 water. Dukes median water temperature is similar to that noted for both water TYPES 3 and 4 and has a median pH similar to that for TYPE 4 water. As noted in the site descriptions, water from B-67 has been linked by fluorescent dye tracing (Rhodamine WT) to Dukes and as such, water at Dukes appears to be a slightly diluted version of water from B-67.

Three of the minor tributary streams have median conductivity values reasonably similar to those noted for TYPE 2 water with the Murrindal River and Spring Creek having median conductivity's similar to TYPE 1 water. The classification of these four types of water and the sites included in the different water types are discussed in more detail in the section dealing with the results of the chemical analyses.

MISCELLANEOUS SITES

As the number of water samples collected from this wide variety of sites with different water types (seeps, intermittent streams, cave waters and flood waters etc.) is limited, the results obtained will only be discussed

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briefly and in relation to the results found for the sites sampled in the previous two sections. From the results presented in Table 4.3 the <u>in-situ</u> field measurements made for this group of sites were generally within the range of values obtained for the major surface and minor tributary streams and the karst spring and cave water sites.

Un-named Seep (Site 18) - small seep located in same outlier of Buchan Caves Limestone as New Guinea 2 and New Guinea 6 and is unusual in that the median pH and conductivity differ quite markedly when compared to the respective medians for the two New Guinea sites, particularly in the case of conductivity which is notably higher; median water temperature similar to the median for these two sites.

Un-named Creek (Site 19) - intermittent surface stream that only flows after heavy rain with flow most likely connecting into the Scrubby Creek cave system; median water temperature, pH and conductivity similar to those noted at Scrubby Creek 2.

Butchers Creek (Site 20) - minor tributary stream to the Murrindal River with median values for all parameters, except water temperature, similar to

TABLE 4.3. RESULTS OF IN-SITU MEASUREMENTS OF WATER TEMPERATURE (°C), Eh (mV), pH AND CONDUCTIVITY (µS cm-1 25°C) FOR MISCELLANEOUS SITES (SITE NUMBERS AS IN TABLE 3.1). RANGE, MEDIAN, SEMI INTER-QUARTILE RANGE (S.I.Q.), MEAN, STANDARD DEVIATION (S.D.) AND SKEWNESS VALUES GIVEN ONLY FOR SITES WHERE n ≥ 4 OTHERWISE RANGE OF VALUES OR VALUE ONLY GIVEN (n = NUMBER OF SAMPLES).

SITE NO.		WATER TEMPERATURE (°C)	Eh (mV)	pH	CONDUCTIVITY (µS cm-1 25°C)
18)	range	9.5 - 19.0	385 - 431	6.70 - 7.13	302 - 1001
	median	14.5	410	7.11	805
	S.I.Q.	3.5	3	0.04	43
	mean	14.8	409	7.02	726
	S.D.	4.2	16	0.18	259
	skewness	-0.08	-0.16	-1.40	-0.89
	n =	(5)	(5)	(5)	(5)
19)	range	11.0 - 19.0	403 - 423	7.15 - 8.05	455 - 499
	median	16.5	412	7.64	-
	S.I.Q.	3.3	7	0.38	-
	mean	15.8	412	7.62	-
	S.D.	4.0	8	0.44	-
	skewness	-0.28	0.27	-0.06	-
	n =	(4)	(4)	(4)	(3)
20)	range	7.0 - 21.0	414 - 428	7.10 - 8.12	161 - 270
	median	13.8	-	7.30	180
	S.I.Q.	3.7	-	0.29	34
	mean	13.9	-	7.46	198
	S.D.	5.8	-	0.46	50
	skewness	0.09	-	0.97	0.91
	n =	(4)	(2)	(4)	(4)
21)	range	11.0 - 20.0	405 - 421	7.08 - 7.86	258 - 380
	median	16.0	-	7.35	291
	S.I.Q.	2.5	-	0.17	32
	mean	16.0	-	7.46	303
	S.D.	3.7	-	0.31	51
	skewness	-0.24	-	0.14	0.64
	n =	(5)	(3)	(5)	(5)
22a)	range	11.5 - 15.3	398 - 425	6.89 - 7.39	289 - 460
	n =	(3)	(2)	(3)	(3)
22b)	value	15.8	n.a.	7.16	1027
22c)	range	13.9 - 18.0	n.a.	7.54 - 7.91	301 - 1487
	median	16.4	-	7.58	1227
	S.I.Q.	1.1	-	0.04	102
	mean	16.1	-	7.55	1186
	S.D.	1.7	-	0.18	521
	skewness	-0.26	-	-0.21	-1.02
	n =	(4)	-	(4)	(4)
23)	range	10.5 - 16.8	n.a.	7.10 - 7.55	354
	n =	(2)	-	(2)	(1)
24)	range	11.0 - 13.0	407 - 437	7.40 - 7.63	212
	n =	(2)	(2)	(2)	(1)
25)	value	11.5	n.a.	7.60	n.a.
26)	value	16.0	428	7.88	390
27)	value	15.0	421	7.61	241
28)	value (i)	28.0	n.d.	7.96	283
	" (ii)	23.0	317	7.96	247

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TABLE 4.3 (cont.)

29)	value	16.5	380	7.93	149
30)	value	8.0	n.a.	7.02	197
31)	value	11.0	n.a.	7.10	n.a.
32)	range n =	17.0 - 19.0 (2)	398 - 413 (2)	7.68 - 7.81 (2)	845 - 924 (2)
33)	value	9.0	n.a.	5.64	n.a.

the medians observed for the major surface stream sites.

Sub-Aqua (Site 21) - resurgence of the Murrindal River with medians for water temperature and conductivity similar to the respective medians for the Murrindal River; slightly lower median pH than that observed for the Murrindal River.

With the remaining sites the results obtained are better discussed in the context in which the measurements were made and a better understanding is achieved when the results of the chemical analyses for these sites are discussed with the results obtained from the other sites sampled, in particular the karst spring and cave water sites.

CHEMICAL ANALYSES.

The range, median, S.I.Q., mean, S.D. and skewness values for Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-}, SO_4^{2-}, alkalinity and total hardness are given in Tables 4.4, 4.5 and 4.6 for the water samples collected and analysed from the major surface and minor tributary stream sites, karst spring and cave water sites and the miscellaneous sites respectively. Total hardness values are calculated from the Ca^{2+} and Mg^{2+} values found for each water sample collected by multiplying by the appropriate factor to obtain equivalent calcium carbonate concentrations (A.P.H.A., 1976), i.e.,

$$\text{Total Hardness (mg/l } CaCO_3) = (Ca^{2+} \times 2.497) + (Mg^{2+} \times 4.116)$$

Also presented in Table 4.4 are the range, median, S.I.Q., mean, S.D. and skewness values for the above parameters obtained from chemical data available from the R.W.C. for the Buchan River at Buchan (1978-88) and the Snowy River at Jarrahmond (1977-85).

MAJOR SURFACE AND MINOR TRIBUTARY STREAM SITES

MAJOR SURFACE STREAMS

Of the three major surface stream sites sampled the Buchan River showed the greatest range for nearly all chemical parameters and also had the lowest medians for most parameters. Of the other two major surface stream sites, the Snowy River had the smallest range in values, while the Murrindal River recorded the highest medians for all parameters.

TABLE 4.9. RESULTS OF CHEMICAL ANALYSES (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-}, $SO4^{2-}$, ALKALINITY AND TOTAL HARDNESS) FOR MAJOR AND MINOR TRIBUTARY STREAMS (SITE NUMBERS AS IN TABLE 3.1). RANGE, MEDIAN, SEMI INTER QUARTILE RANGE (S.I.Q.), MEAN, STANDARD DEVIATION (S.D.), AND SKEWNESS VALUES GIVEN (n = NUMBER OF SAMPLES). ALL PARAMETERS mg/l, EXCEPT ALKALINITY AND TOTAL HARDNESS WHICH ARE AS mg/l $CaCO_3$. DATA FOR BUCHAN (##) AND SNOWY (**) RIVERS FROM R.W.C..

SITE NO.		Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Cl^{-}	$SO4^{2-}$	Alkalinity	Total Hardness
MAJOR SURFACE STREAMS									
1)	range	2.4 - 70.1	1.2 - 16.5	3.5 - 29.9	0.7 - 5.4	4.0 - 68.4	<0.5 - 3.7	17.2 - 207.2	10.9 - 234.8
	median	7.4	2.8	6.7	1.4	8.0	2.1	33.0	29.8
	S.I.Q.	2.3	0.5	1.7	0.4	3.0	1.6	8.3	6.1
	mean	11.5	4.1	9.3	1.5	14.3	2.1	46.8	45.3
	S.D.	14.8	4.1	5.7	1.4	17.6	1.6	42.7	51.3
	skewness	3.32	2.41	2.06	2.66	2.47	0.03	2.92	2.86
	n =	(20)	(20)	(20)	(20)	(20)	(9)	(20)	(20)
2)	range	3.9 - 54.7	1.4 - 16.5	7.9 - 23.8	1.5 - 4.7	10.0 - 46.2	2.9 - 6.0	20.8 - 194.8	15.5 - 204.5
	median	20.2	8.7	16.7	2.8	32.9	3.8	76.8	93.7
	S.I.Q.	2.9	2.0	1.1	0.5	2.9	0.3	11.3	13.6
	mean	22.5	9.3	16.2	2.9	32.5	4.2	86.3	94.6
	S.D.	9.8	3.2	3.4	0.9	7.9	1.8	34.2	35.9
	skewness	1.66	-0.10	-0.42	0.51	-0.94	0.63	1.54	1.05
	n =	(19)	(19)	(19)	(19)	(19)	(5)	(19)	(19)
3)	range	4.6 - 12.0	3.7 - 9.2	8.1 - 16.7	0.7 - 2.3	13.0 - 27.6	1.2 - 4.3	27.1 - 68.7	31.0 - 66.6
	median	9.5	7.3	13.1	1.8	17.4	3.1	52.7	52.9
	S.I.Q.	1.6	1.6	2.2	0.4	3.9	1.2	10.8	10.5
	mean	9.1	7.1	12.4	1.6	18.2	3.0	54.1	51.7
	S.D.	2.4	1.9	2.9	1.2	4.8	1.4	13.3	13.1
	skewness	-0.52	-0.33	-0.12	-0.56	0.66	-0.21	-0.15	-0.38
	n =	(10)	(10)	(10)	(10)	(10)	(5)	(10)	(10)
##)	range	2.3 - 80.0	1.2 - 28.0	3.1 - 38.0	0.7 - 2.7	3.0 - 98.0	-	15.0 - 240.0	11.0 - 300.0
	median	7.0	2.9	6.6	1.2	7.3	-	34.0	31.5
	S.I.Q.	3.0	0.4	0.7	0.3	2.3	-	10.5	11.5
	mean	9.8	3.5	7.2	1.2	9.9	-	40.6	41.5
	S.D.	12.6	4.2	5.6	0.5	15.2	-	36.5	46.4
	skewness	5.00	5.70	4.84	1.13	5.64	-	4.48	4.76
	n =	(38)	(38)	(38)	(38)	(38)	-	(38)	(38)

TABLE 4.4 (CONT.).

3)	range	4.6 - 15.0	3.2 - 14.0	1.2 - 17.0	0.5 - 19.0	3.0 - 27.0	-	24.0 - 72.0	24.6 - 82.7
	median	9.2	6.1	11.0	1.2	16.0	-	46.0	49.4
	S.I.Q.	2.3	1.5	2.1	0.3	3.0	-	7.2	8.1
	mean	10.5	6.4	10.7	1.7	15.6	-	48.2	52.3
	S.D.	2.8	1.9	3.2	2.6	4.7	-	14.4	14.5
	skewness	0.25	1.00	-0.40	6.37	-0.06	-	0.56	0.61
	n =	(26)	(26)	(26)	(24)	(26)	(21)	(24)	(26)
MINOR TRIBUTARY STREAMS									
4)	range	3.0 - 144.4	2.1 - 29.9	13.6 - 47.0	2.0 - 10.3	14.0 - 114.9	0.5 - 10.4	28.4 - 455.4	20.4 - 481.6
	median	17.7	13.0	28.7	4.6	62.9	4.2	70.1	98.9
	S.I.Q.	12.9	3.1	5.0	1.4	14.8	3.3	42.3	40.9
	mean	33.2	13.5	28.1	5.1	59.5	4.6	120.9	138.4
	S.D.	38.5	7.3	8.8	2.2	23.8	3.7	117.9	123.6
	skewness	1.70	0.72	0.02	0.82	-0.03	0.42	1.46	1.52
	n =	(23)	(23)	(23)	(23)	(23)	(9)	(23)	(23)
5)	range	3.9 - 95.8	2.1 - 43.1	12.3 - 39.6	1.0 - 6.5	18.0 - 87.0	<0.5 - 9.9	22.8 - 359.9	18.4 - 405.9
	median	68.2	36.6	29.6	1.8	64.4	8.3	302.5	326.5
	S.I.Q.	17.8	6.5	4.7	0.8	13.5	2.5	54.1	71.2
	mean	61.5	30.7	29.4	2.6	57.4	7.0	253.0	279.9
	S.D.	29.1	13.4	8.8	1.9	20.2	3.7	111.4	126.8
	skewness	-0.75	-1.13	-0.84	1.25	-0.63	-0.96	-1.08	-0.96
	n =	(10)	(10)	(10)	(10)	(10)	(6)	(10)	(10)
6)	range	72.1 - 91.4	10.9 - 13.7	31.0 - 45.0	1.1 - 4.5	54.0 - 76.0	13.0 - 19.3	209.0 - 262.2	225.9 - 281.7
	median	80.0	12.3	37.9	2.9	62.1	16.0	231.8	250.0
	S.I.Q.	4.7	0.4	1.1	0.5	1.8	0.3	11.8	12.6
	mean	80.6	12.4	38.1	2.9	63.2	16.0	234.0	252.4
	S.D.	6.5	0.8	3.3	0.9	5.5	2.1	17.0	18.0
	skewness	0.22	-0.38	-0.11	-0.17	0.88	0.26	0.14	0.16
	n =	(11)	(11)	(11)	(10)	(11)	(11)	(11)	(11)
7)	range	72.3 - 101.2	6.3 - 8.4	9.8 - 20.0	0.9 - 2.0	30.6 - 36.4	4.0 - 4.9	196.9 - 270.2	214.3 - 284.4
	median	87.8	7.8	16.1	1.4	33.0	-	227.0	249.8
	S.I.Q.	3.1	0.3	1.2	0.3	1.1	-	8.9	6.5
	mean	87.7	7.7	15.7	1.5	33.3	-	231.5	250.8
	S.D.	7.7	0.6	2.6	0.4	2.0	-	19.6	18.3
	skewness	-0.34	-1.02	-0.70	-0.04	0.39	-	0.18	-0.21
	n =	(13)	(13)	(13)	(12)	(13)	(3)	(13)	(13)

The range of values, and associated medians, found in this study (for all chemical parameters) for the Buchan and Snowy Rivers, are reasonably similar to the range and medians noted in the chemical data obtained from the R.W.C. for these sites.

The highest chemical ion concentrations found for the Buchan and Murrindal Rivers over the study period are associated with water samples collected in February 1983 (as noted in Chapter Three both streams had ceased to flow). The increase in chemical ion concentrations is certainly more noticeable (when compared to median chemical ion values) for the Buchan River than for the Murrindal River. Chemical values for the Buchan River are between 3.7 (for Na^+) and 9.5 (for Ca^{2+}) times higher than the respective medians and assuming Cl^- displays "conservative behaviour" (see discussion in Chapter Five) are assumed to be due to concentration by evaporation (based on almost 9 fold increase in Cl^-) rather than dominance by ground water input.

For the Murrindal River the February 1983 chemical ion values are between 1.3 (for Cl^-) and 2.7 (for Ca^{2+}) times higher than the respective medians and based on the above reasoning possibly indicates either dominance by ground water input or increased dissolution of carbonate material rather than concentration by evaporation. For the Snowy River the February 1983 chemical levels were only slightly higher than the medians observed for most chemical parameters at this site. The chemical data obtained from the R.W.C. for the Buchan and Snowy Rivers (February 1983) shows very similar trends to that observed in the results for this study, i.e. highest values on record for most chemical parameters were recorded for the Buchan River, whereas most chemical parameters for the Snowy River were only slightly higher than the respective median values.

The chemical data obtained from water samples collected in July 1984 (high flow event) for the Murrindal River were the lowest values recorded at this site over the study period (with the exception of K^+), whereas for the Buchan and Snowy Rivers lower chemical values for most parameters were recorded on one or two other occasions.

Using ionic proportions (in meq/l) of the median values obtained for these three sites for both cations and anions (alkalinity is assumed to be same as HCO_3^-, i.e. HCO_3^- (mg/l) obtained by multiplying alkalinity as mg/l $CaCO_3$ by 1.219 – Wigley (1977, p.6)). For the three sites HCO_3^- is the dominant anion with Cl^- accounting for between 24.3%-36.5% of the total anion concentration and SO_4^{2-} usually contributing < 5.0%. For the cations, K^+ accounts for < 4.5% of the total cation concentration with the relative ionic proportions of the other cations varying from site to site:- Buchan River, $Ca^{2+} > Na^{+} > Mg^{2+}$; Murrindal River, $Ca^{2+} > Na^{+} \approx Mg^{2+}$ and Snowy River, $Mg^{2+} \approx Na^{+} > Ca^{2+}$.

Comparing the cationic and anionic composition of the water samples collected under low flow and high flow conditions, it is interesting to note that for all three sites Na^{+} is the dominant cation (45.6%-47.9%) under high flow conditions, with $Ca^{2+} \approx Mg^{2+}$ for the Buchan and Snowy Rivers, and $Ca^{2+} > Mg^{2+}$ for the Murrindal River, with K^{+} accounting for 4.0%-8.9% of the total cation concentration.

Under low flow conditions (February 1983) a dramatic change is noticed in which for the Buchan and Murrindal Rivers, Ca^{2+} and Mg^{2+} ions account for 79.7% and 78.9% of the cation concentration (meq/l) respectively, with Na^{+} contributing ≈ 20% and K^{+} contributing ≈ 1.0%. For the Snowy River under low flow conditions the cationic order of dominance is Mg^{2+} (37.5%) > Na^{+} (31.0%) ≈ Ca^{2+} (28.8%) > K^{+} (2.7%) which is similar to the median order of cation dominance.

In the case of the anions (only Cl^{-} and HCO_3^{-} considered), under both flow regimes HCO_3^{-} is the dominant anion for all three sites, but actual percentage contribution of Cl^{-} increases under high flow conditions e.g. Murrindal River, Cl^{-} contribution to total anion concentration varies from 24.0% (low flow) to 40.0% (high flow).

The usual cationic and anionic order of dominance in the majority of Australian fresh and lentic waters is according to Williams (1967), $Na^+ > Mg^{2+} > Ca^{2+} > K^+ : Cl^- > HCO_3^- > SO_4^{2-}$, but as noted by Hart and McKelvie (1986) in a review of chemical limnology in Australia, one must be aware of the vast range of geographic and climatic differences existing. In summing they concluded that most Australian streams are dominated by sodium and bicarbonate ions, although chloride can often be similar in dominance to bicarbonate in headwater streams. They also noted that the fast flowing permanent coastal streams in Eastern Australia are "rainfall dominated" i.e. most of the salts come from the atmosphere, whereas inland flowing streams tend to be more "rock dominated" in their lower reaches, with higher proportions of Ca^{2+}, Mg^{2+} and HCO_3^- due to the interaction between rainfall and catchment lithology.

For the surface streams sampled in this study catchment lithology appears to be of more importance in determining streamwater chemistry than atmospheric contribution but the switch to Na^+ dominance under high flow conditions is consistent with the known surface pathways of flood waters.

MINOR TRIBUTARY STREAMS

For the minor tributary stream sites, Spring Creek showed the greatest range of values for all parameters except Mg^{2+} and had the lowest medians for Ca^{2+}, $SO_4{}^{2-}$, alkalinity and total hardness. In terms of median values for most chemical parameters Spring Creek is closer in terms of water chemistry to Murrindal River water than water sampled from the other minor tributary streams. Interestingly, the relative ionic proportions of the median cation and anion values for Spring Creek ($Na^+ > Mg^{2+} > Ca^{2+} >> K^+ : Cl^- > HCO_3{}^- >> SO_4{}^{2-}$) are more typical of Williams's (1967) description of Australian fresh waters, although the actual values in mg/l are quite high when compared to the median chemical values found for the Buchan and Snowy Rivers.

For the other minor tributary streams, catchment lithology is assumed to be of prime importance in determining water chemistry e.g. alkalinity (as $HCO_3{}^-$) accounts for between 69.0% - 83.0% of the total relative anionic proportions (median values), with Ca^{2+} and Mg^{2+} accounting for 74.3% to 87.2% of the total median cation concentration. This lithology effect is examined in more detail in Chapter Five.

When comparing the chemical data as a whole for both groups, and if the median values obtained for the Buchan River are taken as background readings for an area of uniform lithology, rainfall etc., the minor tributary streams all show increased chemical levels (using median values) for practically all parameters and this primarily is attributed to the presence of the more soluble carbonate material in the catchments of these sites.

Discharge obviously influences chemical ion concentrations and it interesting to note that four of the five sites sampled in July 1984 (Buchan River, Murrindal River, Spring Creek and Back Creek) had relatively similar total hardness values ranging from 14.2mg/l (Buchan River) to 20.4mg/l (Spring Creek) with the Snowy River being higher at 31.0mg/l. As noted in the <u>in-situ</u> field measurement section these same four sites recorded similar water temperature and pH values which reinforces the idea of the high flow water being of the same source i.e surface runoff.

Of the four sites in this group, only Spring Creek was sampled in February 1983 and the relative ionic proportions noted for water samples collected at this time for the Buchan and Murrindal Rivers are very similar to those observed at Spring Creek, i.e. Ca^{2+} and Mg^{2+} account for ≈ 77% of the total cation concentration (meq/l) with HCO_3^- accounting for ≈ 74% of the total anion concentration.

Only two sites in this group, Spring Creek and Back

Creek, were sampled in July 1984 (high flow conditions) and the order of cation dominance is almost identical for both sites, for Spring Creek - Na^+ (55.7%) > Ca^{2+} (22.0%) > Mg^{2+} (16.2%) > K^+ (6.0%) and for Back Creek - Na^+ (55.7%) > Ca^{2+} (20.2%) > Mg^{2+} (17.9%) > K^+ (6.1%). For the anions however the relative ionic proportions are different, for Spring Creek HCO_3^- (60.3%) is dominant whereas for Back Creek the Cl^- and HCO_3^- contributions are relatively similar i.e. 52.7% and 47.3% respectively.

For Spring Creek the relative proportions of the median anion values indicate that water at this site is usually Cl^- dominated, yet the chemical data for both February 1983 and July 1984 indicates that HCO_3^- is the dominant anion. The high flow chemical results for Back Creek were the lowest recorded whereas for Spring Creek lower chemical levels were recorded on one other occasion.

KARST SPRING AND CAVE WATER SITES

The data presented in Table 4.5 shows that water chemistry varies considerably from site to site and for the majority of sites that have been monitored the most over the study period a wide range of results are noted.

As noted previously in the section dealing with the *in-situ* field measurements, the sites sampled in this group, were on the basis of similar medians divided into four different groups each of a particular water TYPE. The median chemical values obtained and the range of values observed adds further weight to this subjective classification of the sites into the different water types.

TYPE 1 – New Guinea 2 and New Guinea 6: lowest median values for most chemical parameters and are generally closer to the medians observed for the Murrindal River and Spring Creek than those noted at the other sites in this group. In terms of ionic proportions (median values in meq/l), TYPE 1 water is predominantly a Ca^{2+} – HCO_3^- type water (≈ 55% and 75% respectively) with Na^+ (≈ 25%) > Mg^{2+} (≈ 18%) >> K^+ (≈ 3%) and for the anions Cl^- (≈ 21%) >> SO_4^{2-} (≈ 3%).

TYPE 2 – M-4 and Scrubby Creek 1, 2 and 3: median Ca^{2+}, alkalinity and total hardness values are approximately 3-4 times the respective medians noted for TYPE 1 water. Water is dominated by the ions Ca^{2+} and HCO_3^- with the relative contributions being 71.6% and 83.2% (M-4) and 78.6% and 84.0% (Scrubby Creek 2) respectively. Higher median Mg^{2+}, Na^+, Cl^- and SO_4^{2-} values than those noted for TYPE 1 water, although when expressed as relative cation and anion proportions the

TABLE 4.5. RESULTS OF CHEMICAL ANALYSES (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-}, SO_4^{2-}, ALKALINITY AND TOTAL HARDNESS) FOR KARST SPRING AND CAVE WATER SITES (SITE NUMBERS AS IN TABLE 3.1). RANGE, MEDIAN, SEMI INTER QUARTILE RANGE (S.I.Q.), MEAN, STANDARD DEVIATION AND SKEWNESS VALUES GIVEN (n = NUMBER OF SAMPLES). ALL PARAMETERS mg/l EXCEPT ALKALINITY AND TOTAL HARDNESS WHICH ARE AS mg/l $CaCO_3$.

SITE NO.		Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Cl^{-}	SO_4^{2-}	Alkalinity	Total Hardness
8)	range	20.2 - 70.1	2.6 - 12.6	8.1 - 20.0	1.7 - 7.5	17.0 - 21.0	2.0 - 8.6	69.2 - 225.1	61.4 - 226.9
	median	25.3	4.8	13.5	2.5	19.5	5.0	90.0	88.9
	S.I.Q.	10.9	3.1	2.0	0.9	1.3	2.1	33.4	37.1
	mean	34.0	6.4	13.4	3.3	19.9	4.9	119.7	110.9
	S.D.	19.1	3.8	3.6	2.0	2.2	2.6	64.4	62.3
	skewness	1.17	0.68	0.39	1.42	0.58	0.18	0.94	1.11
	n =	(8)	(8)	(8)	(8)	(8)	(6)	(7)	(8)
9)	range	14.0 - 73.5	2.4 - 13.1	7.9 - 23.5	1.4 - 4.3	16.0 - 22.0	2.0 - 7.8	59.4 - 226.9	44.8 - 237.4
	median	27.1	5.4	13.4	3.0	19.2	3.2	95.8	92.4
	S.I.Q.	16.3	1.7	2.0	1.1	2.0	1.1	41.4	46.2
	mean	33.6	6.1	14.0	2.8	18.8	4.0	128.5	109.1
	S.D.	21.3	3.3	2.7	1.2	2.3	2.1	59.8	65.9
	skewness	0.80	1.17	0.88	-0.07	-0.03	1.06	0.79	0.90
	n =	(8)	(8)	(8)	(8)	(8)	(6)	(6)	(8)
10)	range	11.9 - 104.0	2.9 - 23.1	12.1 - 39.5	1.3 - 4.9	21.0 - 85.5	<0.5 - 11.6	48.1 - 335.2	41.7 - 354.8
	median	73.5	14.6	21.7	2.8	41.0	9.8	209.0	237.0
	S.I.Q.	25.4	4.3	1.9	0.6	5.5	3.9	75.2	76.5
	mean	60.5	13.0	21.2	2.8	41.8	7.4	187.7	204.5
	S.D.	30.8	5.3	5.0	0.9	13.5	4.2	88.7	97.1
	skewness	-0.31	-0.09	1.51	0.62	1.56	-0.55	-0.17	-0.32
	n =	(29)	(29)	(29)	(28)	(29)	(10)	(29)	(29)
11)	range	35.8 - 110.6	2.7 - 16.1	9.5 - 19.8	1.6 - 3.6	19.0 - 40.0	<0.5 - 11.1	93.4 - 303.5	100.5 - 342.4
	median	98.9	14.1	16.9	2.6	37.0	9.5	281.5	303.7
	S.I.Q.	4.1	0.9	1.4	0.6	2.4	3.1	17.4	14.5
	mean	91.6	13.1	16.1	2.6	35.5	8.2	257.2	282.6
	S.D.	21.3	3.4	2.6	0.6	5.4	3.8	59.8	65.2
	skewness	-1.46	-2.09	-1.20	-0.06	-1.98	-0.96	-1.66	-1.67
	n =	(18)	(18)	(18)	(18)	(18)	(9)	(18)	(18)
12a)	range	49.1 - 125.0	2.8 - 9.9	9.9 - 21.8	0.9 - 2.3	19.0 - 37.8	4.0 - 11.9	129.7 - 334.0	134.1 - 341.2
	median	102.7	7.8	16.1	1.5	31.1	5.6	261.5	285.1
	S.I.Q.	16.3	1.3	2.1	0.4	6.0	2.3	36.7	35.8
	mean	98.9	6.9	16.0	1.6	29.9	6.5	259.5	275.4
	S.D.	24.2	2.1	3.3	0.5	6.6	2.8	62.9	65.8
	skewness	-0.76	-0.69	-0.14	0.16	-0.44	1.00	-0.72	-0.95
	n =	(12)	(12)	(12)	(12)	(12)	(8)	(12)	(12)
12b)	range	27.0 - 124.5	1.1 - 10.4	8.3 - 20.0	1.0 - 3.0	9.0 - 38.1	<0.5 - 13.2	80.0 - 320.6	71.9 - 343.8
	median	97.8	7.8	16.0	1.5	33.0	5.0	258.5	279.6
	S.I.Q.	10.3	1.1	1.9	0.3	2.0	1.5	24.0	24.1
	mean	94.7	7.2	15.2	1.6	30.3		250.4	266.2
	S.D.	23.4	2.2	3.1	0.5	7.3	3.8	58.9	65.1
	skewness	-1.37	-1.30	-0.71	1.10	-1.54	0.56	-1.48	-1.59
	n =	(22)	(22)	(22)	(20)	(22)	(9)	(22)	(22)

TABLE 4.5 (CONT.).

12c)	range	27.0 - 111.1	1.1 - 10.3	8.3 - 20.0	1.0 - 3.2	9.0 - 36.8	<0.5 - 10.3	80.0 - 285.4	71.9 - 310.8
	median	88.0	7.9	16.1	1.5	32.5	4.7	231.5	250.7
	S.I.Q.	11.6	1.0	2.1	0.4	4.0	2.2	22.5	20.9
	mean	83.1	7.0	15.3	1.7	29.8	5.4	222.2	238.0
	S.D.	19.8	2.2	3.3	0.6	7.3	3.2	48.9	55.7
	skewness	-1.26	-1.30	-0.71	1.13	-1.45	0.17	-1.37	-1.63
	n =	(20)	(20)	(20)	(19)	(20)	(10)	(21)	(20)
13)	range	99.6 - 126.7	16.5 - 41.4	13.8 - 39.3	0.8 - 2.6	17.0 - 68.0	2.0 - 13.6	330.4 - 426.2	326.4 - 474.0
	median	121.2	37.1	28.8	1.5	61.2	11.9	413.6	459.0
	S.I.Q.	4.2	2.7	1.8	0.3	2.4	5.0	4.5	14.7
	mean	118.6	35.2	27.8	1.5	57.4	8.7	405.7	441.1
	S.D.	7.5	6.1	5.5	0.5	11.8	5.1	26.6	41.0
	skewness	-1.23	-1.92	-0.76	0.44	-2.43	-0.60	-2.24	-1.87
	n =	(20)	(20)	(20)	(20)	(20)	(9)	(20)	(20)
14)	range	60.5 - 178.3	10.8 - 36.2	28.7 - 90.0	1.6 - 5.2	60.0 - 256.0	4.2 - 24.3	165.4 - 397.0	199.6 - 594.2
	median	157.8	30.5	77.0	3.0	211.0	15.0	364.9	522.2
	S.I.Q.	17.0	2.4	4.5	0.5	10.4	4.5	12.0	33.4
	mean	144.6	29.0	70.2	3.1	195.2	11.6	342.2	480.6
	S.D.	32.0	7.5	16.3	0.7	54.7	5.5	63.2	110.2
	skewness	-1.66	-1.41	-1.57	0.51	-1.52	-0.44	-1.88	-1.62
	n =	(31)	(31)	(31)	(30)	(31)	(13)	(31)	(31)
15)	range	107.8 - 128.1	12.9 - 25.5	31.9 - 66.3	2.2 - 3.4	99.3 - 203.0	-	220.9 - 279.7	324.3 - 424.8
	median	120.5	22.9	57.8	3.0	180.5	-	235.6	393.1
	S.I.Q.	7.8	0.9	2.9	0.3	9.7	-	9.2	11.8
	mean	118.2	21.7	56.1	2.9	175.4	-	237.7	384.5
	S.D.	8.7	4.1	11.3	0.4	35.3	-	20.6	33.0
	skewness	-0.14	-1.59	-1.58	-0.67	-1.64	-	1.29	-0.70
	n =	(7)	(7)	(7)	(6)	(7)		(7)	(7)
16)	range	42.2 - 188.6	6.8 - 44.2	23.7 - 111.1	1.9 - 5.0	41.0 - 313.0	3.1 - 33.3	116.9 - 411.4	133.4 - 644.8
	median	177.6	39.9	104.2	3.1	300.2	23.9	404.5	611.0
	S.I.Q.	5.8	1.6	3.6	0.5	6.0	5.3	4.3	22.9
	mean	170.3	38.0	98.6	3.4	284.2	20.2	384.8	581.9
	S.D.	32.3	7.9	19.0	0.7	59.8	9.7	67.2	112.2
	skewness	-3.23	-3.16	-3.13	0.11	-3.44	-0.29	-3.36	-3.30
	n =	(22)	(22)	(22)	(21)	(22)	(9)	(22)	(22)
17)	range	144.8 - 188.9	34.3 - 43.9	78.5 - 112.0	2.3 - 4.6	225.0 - 314.0	14.1 - 26.8	337.0 - 409.7	502.8 - 643.2
	median	176.4	40.2	103.2	3.5	297.8	-	402.9	597.4
	S.I.Q.	6.0	1.5	3.3	0.5	6.9	-	6.1	20.1
	mean	174.2	39.9	101.1	3.5	291.2	-	396.5	599.2
	S.D.	12.8	2.6	8.4	0.7	22.5	-	20.3	37.6
	skewness	-0.96	-0.34	-1.43	0.01	-2.05	-	-2.16	-1.18
	n =	(13)	(13)	(13)	(12)	(13)	(3)	(13)	(13)

respective ion contribution to the total is smaller.

TYPE 3 - Bitch of a Ditch: Highest median alkalinity of all sites with the respective cation and anion proportions (median values in meq/l) being Ca^{2+} (58.2%) > Mg^{2+} (29.4%) > Na^{+} (12.1%) >> K^{+} (0.4%) and HCO_3^- (81.7%) > Cl^- (17.1%) > SO_4^{2-} (2.5%). Mg^{2+} contribution to the cation total is the highest of all sites in this group and reflects the fact that the catchment of this site is predominantly dolomite. Smallest range in values for nearly all parameters of the sites that have been sampled the most over the study period.

TYPE 4 - B-67 and B-41 (site 17): Highest medians for all parameters except alkalinity. In terms of ionic proportions (median values meq/l) water composition is Ca^{2+} (≈53%) > Na^{+} (≈ 27%) > Mg^{2+} (≈ 20%) >> K^{+} (< 1%) for the cations and Cl^- (≈ 50%) > HCO_3^-(≈ 48%) >> SO_4^{2-} (≈ 3%) for the anions. Although the median values of the cations (excluding K^{+}) are approximately 7-9 times higher than those found for TYPE 1 water, relative ionic proportions are quite similar. It is interesting to note that although the number of water samples collected from B-67 is ≈ double the number collected from B-41, median chemical values for all parameters are virtually the same which is taken to indicate the same body of water.

Of the remaining sites, Moons is certainly closer in terms of median chemical values to TYPE 2 water rather than TYPE 1 water. Median chemical values found at Dukes are closer to those observed for TYPE 4 water than the other water TYPES and this is not unexpected as water from B-67, as noted previously, has been linked by fluorescent dye tracing to the spring outlet at Dukes. The lower medians observed at Dukes indicate dilution by mixing of B-67 water with water or waters of a unknown but lower chemical composition. This can be explained by the fact that Cl- can be termed a "conservative element" and exhibits conservative behaviour (see discussion in Chapter Five), i.e. it is an element where any increase or decrease in concentration can simply be explained in terms of the mixing of ground waters with different Cl- values.

Scrooges Vault water is unusual and perhaps should represent another water type in that although it lies within ≈50m of B-67 AND B-41 (TYPE 4 water) median chemical values are notably lower and for particular parameters lie between medians found for water TYPES 2, 3 and 4. Median cation proportions are very similar to those noted at Dukes although for the anions relative ionic proportions are very similar to those for TYPE 4 water. It was first assumed that water from this site was mixing with B-67 water and exiting at Dukes, but dye tracing experiments from this site has so far been unsuccessful and water three months after an attempted dye trace was still highly coloured with lissamine indicating very slow movement of water at this site. The chemical characteristics of water at Dukes, Scrooges Vault, B-67 and B-41 are discussed in more detail when the spatial variations in median chemical values are examined in Chapter Five.

The behaviour of the karst spring and cave water sites to recharge events operating in their respective catchments and how this water is transmitted through a particular system is examined in Chapter Six.

THE UNIVERSITY OF

MISCELLANEOUS SITES

The results for these sites are presented in Table 4.6 and as noted previously for the results obtained from the *in-situ* field measurements, the results obtained from each particular site are best discussed in terms of the results obtained from the other sites sampled.

Un-named Seep: Notably higher median values for Ca^{2+}, Mg^{2+}, SO_4^{2-}, alkalinity and total hardness than those observed for the two New Guinea sites which are located nearby (Figure 3.1). Ca^{2+} and Mg^{2+}

TABLE 4.6. RESULTS OF CHEMICAL ANALYSES (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-}, SO_4^{2-}, ALKALINITY AND TOTAL HARDNESS) FOR MISCELLANEOUS SITES (SITE NUMBERS AS IN TABLE 3.1). RANGE, MEDIAN, SEMI INTER-QUARTILE RANGE (S.I.Q.), MEAN, STANDARD DEVIATION (S.D.) AND SKEWNESS VALUES GIVEN ONLY FOR SITES WHERE n (NUMBER OF SAMPLES) ≥ 4, OTHERWISE RANGE OR VALUE GIVEN. ALL PARAMETERS mg/1 EXCEPT ALKALINITY AND TOTAL HARDNESS WHICH ARE AS mg/1 $CaCO_3$.

SIT NO.	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Cl^{-}	SO_4^{2-}	Alkalinity	Total Hardness
18) range	31.8 - 121.1	9.2 - 28.2	5.7 - 26.5	1.4 - 3.2	26.9 - 39.0	9.0 - 23.5	101.7 - 385.7	117.3 - 418.3
median	101.9	25.2	18.8	2.1	30.0	15.2	333.9	360.4
S.I.Q.	16.2	1.9	0.1	0.3	2.9	3.1	60.4	47.1
mean	85.6	22.4	19.7	2.3	31.0	16.7	283.5	305.9
S.D.	35.2	7.6	4.0	0.7	5.2	5.7	117.3	118.2
skewness	-0.68	-1.26	1.05	0.19	0.65	-0.13	-0.77	-0.85
n =	(5)	(5)	(5)	(5)	(5)	(5)	(5)	(5)
19) range	18.3 - 94.1	0.8 - 4.8	3.8 - 16.3	0.9 - 3.4	7.3 - 14.0	5.6 - 6.8	55.5 - 249.7	49.0 - 254.7
median	79.6	4.7	10.0	1.1	12.8	-	222.6	217.9
S.I.Q.	19.1	1.1	3.3	0.7	2.1	-	52.3	51.5
mean	67.9	3.8	10.0	1.6	11.7	-	187.6	184.9
S.D.	33.8	2.0	5.1	1.2	3.1	-	89.2	92.2
skewness	-1.08	-1.14	0.03	1.14	-0.91	-	-1.07	-1.03
n =	(4)	(4)	(4)	(4)	(4)	(3)	(4)	(4)
20) range	7.0 - 14.5	5.0 - 10.5	13.5 - 17.0	2.2 - 2.9	28.1 - 50.3	-	30.8 - 51.6	38.1 - 79.4
median	8.9	6.2	14.4	2.8	29.8	-	37.7	47.7
S.I.Q.	2.3	1.8	1.4	0.2	6.2	-	8.3	7.9
mean	9.8	7.0	14.8	2.7	34.5	-	39.4	53.2
S.D.	3.3	2.5	1.7	0.3	10.6	-	10.1	18.5
skewness	0.82	0.79	0.47	-1.08	1.11	-	0.27	0.81
n =	(4)	(4)	(4)	(4)	(4)	-	(4)	(4)
21) range	20.2 - 40.9	6.7 - 9.3	9.2 - 18.4	1.4 - 4.8	21.0 - 35.4	2.0 - 6.2	69.1 - 143.5	83.0 - 140.4
median	29.6	8.1	14.6	3.0	28.6	4.9	98.5	107.3
S.I.Q.	0.9	0.4	1.3	0.7	4.7	0.3	5.7	6.3
mean	29.7	8.1	14.7	3.1	29.0	4.5	99.6	107.6
S.D.	7.4	1.0	3.5	1.3	5.9	1.5	27.4	25.4
skewness	0.39	-0.38	-0.71	-0.05	-0.21	-0.72	0.75	0.57
n =	(5)	(5)	(5)	(5)	(5)	(5)	(5)	(5)
22a) range	17.2 - 21.1	14.5 - 16.5	29.9 - 35.4	3.9 - 5.9	60.0 - 81.0	-	77.8 - 101.0	102.6 - 120.9
n =	(3)	(3)	(3)	(3)	(3)		(3)	(3)
22b) value	121.6	25.7	57.5	2.3	146.0	-	315.5	409.4

TABLE 4.6 (CONT.)

22c)	range	24.1 - 168.4	8.9 - 34.3	28.6 - 84.6	2.6 - 3.9	49.0 - 235.6	-	87.0 - 376.8	96.8 - 561.7
	median	146.1	27.6	73.5	3.4	201.9	-	353.2	478.3
	S.I.Q.	13.5	1.4	11.0	0.6	31.0	-	19.5	36.0
	mean	121.1	24.6	65.0	3.3	172.1	-	292.6	403.8
	S.D.	65.6	11.0	25.1	0.6	83.7	-	137.5	208.4
	skewness	-1.06	-0.85	-0.94	-0.09	-1.00	-	-1.13	-1.03
	n =	(4)	(4)	(4)	(4)	(4)		(4)	(4)
23)	range	59.5 - 79.9	3.4 - 3.6	7.1 - 9.7	0.8 - 1.3	11.0 - 15.7	4.1	155.4 - 222.4	163.4 - 213.5
	n =	(2)	(2)	(2)	(2)	(2)	(1)	(2)	(2)
24)	range	5.9 - 15.6	3.4 - 5.2	9.9 - 18.9	2.7 - 3.4	16.3 - 22.0	14.0	29.2 - 52.9	25.8 - 60.4
	n =	(2)	(2)	(2)	(2)	(2)	(1)	(2)	(2)
25)	value	6.7	2.5	10.0	3.7	15.0	-	30.0	27.1
26)	value	66.9	3.6	11.8	1.2	18.0	8.0	172.4	181.9
27)	value	20.1	5.4	17.1	4.9	21.0	-	78.3	72.4
28)	value i)	4.1	6.7	23.2	12.7	38.0	-	43.9	37.8
	value ii)	2.4	11.1	29.8	12.2	52.9	-	52.6	51.7
29)	value	1.5	1.6	17.0	7.0	14.0	-	33.7	10.3
30)	value	14.0	4.8	16.4	1.3	35.0	-	38.1	54.7
31)	value	23.0	0.5	13.8	5.4	12.0	-	87.5	59.5
32)	range	110.3 - 111.0	36.4 - 38.4	8.8 - 30.8	1.8 - 2.6	62.0 - 63.6	-	398.1 - 402.2	425.2 - 435.2
	n =	(2)	(2)	(2)	(2)	(2)		(2)	(2)
33)	range	0.4 - 0.83	0.05 - 0.12	0.21 - 0.53	0.04 - 0.53	0.56 - 0.73	-	-	-
	n =	(3)	(3)	(3)	(3)	(2)			

(as relative ionic proportions of the median chemical values in meq/l) account for ≈ 90% of the cation total with HCO_3^- accounting for ≈ 85% of the anion total, which is quite different from the results obtained for the two New Guinea sites. In terms of median chemical values and relative ionic proportions found at all other sites, water at this site is relatively similar to that found at Bitch of a Ditch (TYPE 3 water).

Un-named Creek: Median chemical values all slightly lower than those noted for the nearby Scrubby Creek sites. In terms of median ionic proportions water is predominantly a Ca^{2+} – HCO_3^- (82.4% and 92.5% respectively) type water.

Butchers Creek: This tributary stream to the Murrindal River has similar median Ca^{2+}, Mg^{2+}, Na^+ and total hardness values to those for the Snowy River with K^+ and Cl^- medians being ≈ double those for the Snowy River. In terms of relative cation and anion proportions (median values meq/l), order of dominance is Na^+ (37.9%) > Mg^{2+} (30.9%) > Ca^{2+} (26.9%) >> K^+ (4.4%) and Cl^- (52.7%) > HCO_3^- (47.3%) which is almost the same as that noted for Spring Creek water.

Sub-Aqua: This low flow resurgence of the Murrindal

River has, as would be expected, quite similar medians for Mg^{2+}, Na^{+}, K^{+}, Cl^{-} and SO_4^{2-} to those noted for the Murrindal River, although medians for Ca^{2+}, alkalinity and total hardness are marginally higher. This increase (≈10 mg/l, 22mg/l and 14mg/l respectively) between the two sites can be explained in terms of aggressive Murrindal River water sinking (based on SI_{cal} values) and flowing underground through limestone where dissolution, depending upon flow regimes, takes place until water re-emerges with more Ca^{2+} and HCO_3^- in solution.

Spring Creek - Falls (site 22a): Median chemical values noted at Spring Creek sink (site 4, 1.2kms downstream of this site) lie within, or are relatively similar to the range of results found at this site.

Spring Creek - Dukes (site 22b): Ca^{2+}, Mg^{2+}, Na^{+} and K^{+} values similar to the respective medians found for Scrooges Vault, although alkalinity and Cl^{-} values are different.

Spring Creek - Moons (site 22c): Median chemical values quite similar to the medians found at Dukes.

Federal Cave (site 23): Water sample collected in July 1984 had the second highest Ca^{2+} value of all sites sampled. Ca^{2+} – HCO_3^- dominated type water on both sample occasions although relative proportions of minor ions differed, July 1984 – Na^+ (8.9%) > Mg^{2+} (5.9%) >> K^+ (0.7%) and Cl^- (6.4%) > SO_4^{2-} (1.8%), and for February 1988 – Na^+ (8.6%) ≈ Mg^{2+} (8.2%) >> K^+ (0.6%) and Cl^- (12.5%).

Fairy Creek (site 24): Water samples collected in July and September 1984. The high flow sample (July 1984) had chemical values similar to those noted for Spring Creek in which Na^+ and HCO_3^- were the dominant cation and anion respectively. For the September water sample Na^+ (39.2%) ≈ Ca^{2+} (37.1%) > Mg^{2+} (20.4%) >> K^+ (3.3%) and HCO_3^- (58.9%) > Cl^- (31.6%) > SO_4^{2-} (9.5%).

Wilsons Cave (site 25): Water sample collected in July 1984 in which the chemical values were quite similar to the July 1984 values found at Spring Creek and Fairy Creek.

Royal Cave (site 26): Water sample collected in September 1984 in which chemical values were relatively similar to those values obtained in July 1984 for the water sample collected at site 23. Relative ionic proportions (meq/l) are Ca^{2+} (79.9%) >> Na^+ (10.0%) > Mg^{2+} (7.1%) >> K^+ (0.7%) and HCO_3^- (83.6%) >> Cl^- (12.3%) > SO_4^{2-} (4.0%).

Scrubby Creek Above (site 27): Chemical values similar to the median values found for the Murrindal River. Notably lower Ca^{2+} and alkalinity values than those observed 30m downstream at Scrubby Creek 4.

Farm Dams (site 28i) and 28ii)): Two farm dams located near Scrooges Vault, B-67 and B-41 (sites 15, 16 and 17 respectively). Sampled to see if high Na^{+} and Cl^{-} values noted at three above sites could be traced to Tertiary sands and gravels that form part of the catchment in this area. In terms of relative ionic proportions Na^{+} and Cl^{-} are the dominant cation (48.3% and 49.1%) and anion (55.0% and 58.6%) respectively, although relative chemical values at the farm dam sites are certainly much lower than those noted for sites 15, 16 and 17. Of interest is that the K^{+} values found at these two sites are the highest recorded at any of the sites sampled.

Un-numbered Borehole (site 29): Relative ionic proportions (meq/l) are Na^{+} (65.7%) > K^{+} (15.9%) > Mg^{2+} (11.7%) > Ca^{2+} (6.6%) and HCO_3^{-} (63.0%) and Cl^{-} (37.0%). This site was sampled, as were the two previous sites, to see if high Na^{+} and Cl^{-} noted at sites 15, 16 and 17 could be detected at this site. Chemical values similar to the median values observed for the major surface streams.

Tea-Tree Creek (site 30): Chemical values similar to those observed for the major surface streams. Na^+–Ca^{2+} – Cl^- type water.

Overland Flow (site 31): Surface runoff sample collected in July 1984 draining from Pyramids Marlstone in which Ca^{2+} (59.6%) and HCO_3^- (83.3%) are the dominant cation and anion respectively. Higher Ca^{2+} and alkalinity values than those noted for other surface stream sites sampled on this occasion.

Bitch of a Ditch Below (site 32): Site sampled on two occasions to see if Ca^{2+} and alkalinity levels noted at Bitch of a Ditch decreased downstream away from the spring outlet. Ca^{2+} values decreased by ≈ 8% and alkalinity by ≈ 6% with the other chemical parameters remaining virtually constant. Decrease in Ca^{2+} and HCO_3^- values attributed to calcium carbonate deposition as tufa.

Rainwater (site 33): Rainwater samples collected on three occasions with chemical values of Ca^{2+}, Mg^{2+}, Na^+, K^+ and Cl^- only.

COMPUTED PARAMETERS

The range and medians obtained for $\log(PCO_2)$, SI_{cal}

and SI_{dol} are given in Tables 4.7, 4.8 and 4.9 for the water samples collected from the major surface and minor tributary streams, the karst spring and cave water sites and the miscellaneous sites respectively. The parameters $\log(PCO_2)$ (the theoretical partial pressure of CO_2 with which the water sampled is in equilibrium), SI_{cal} (the saturation index with respect to calcite) and SI_{dol} (the saturation index with respect to dolomite) are obtained by processing the results obtained from both the ***in-situ*** field measurements and the chemical analyses by using the chemical speciation program WATSPEC (Wigley, 1977). The saturation index is a measure of the saturation state of the water sampled with respect to a solid mineral phase (see Chapter One). Briefly, a negative index indicates undersaturation, a positive index indicates super-saturation and a value of 0.00 indicates that the water sampled is in equilibrium with that particular mineral phase.

MAJOR SURFACE AND MINOR TRIBUTARY STREAM SITES

Median $\log(PCO_2)$ values ranged from −2.98 (Snowy River) to −2.07 (Back Creek), with Spring and Tara Creeks having the greatest and smallest range respectively (Table 4.7). The Buchan and Snowy Rivers (median $\log(PCO_2)$ values of −2.98 and −2.96) are the closest of the sites sampled to the atmospheric $\log(PCO_2)$ value of ≈ −3.5, i.e they contain ≈ 3 times more CO_2 than the

TABLE 4.7. RESULTS OF COMPUTED PARAMETERS (LOG(PCO_2), SI_{cal} and SI_{dol}) FOR MAJOR SURFACE AND MINOR TRIBUTARY STREAMS (SITE NUMBERS AS IN TABLE 3.1). RANGE AND MEDIANS GIVEN (n = NUMBER OF SAMPLES). Log(PCO_2) AS ATMOSPHERES; SI_{cal} AND SI_{dol} DIMENSIONLESS.

SITE NO.	Log(PCO_2)	SI_{cal}	SI_{dol}
MAJOR SURFACE STREAMS			
1) range	(-3.63) - (-2.10)	(-2.27) - (0.90)	(-4.70) - (1.61)
median	-2.92	-1.40	-3.16
n =	(20)	(20)	(20)
2) range	(-3.07) - (-2.04)	(-2.22) - (0.90)	(-4.81) - (1.61)
median	-2.65	-0.63	-1.48
n =	(19)	(19)	(19)
3) range	(-3.25) - (-2.44)	(-1.81) - (0.04)	(-3.41) - (0.29)
median	-2.98	-1.03	-2.02
n =	(10)	(10)	(10)
MINOR TRIBUTARY STREAMS			
4) range	(-3.23) - (-1.53)	(-2.26) - (0.42)	(-4.34) - (0.33)
median	-2.61	-1.05	-2.09
n =	(23)	(23)	(22)
5) range	(-2.88) - (-1.44)	(-2.28) - (0.83)	(-4.75) - (1.47)
median	-2.07	0.24	0.32
n =	(10)	(10)	(10)
6) range	(-2.49) - (-1.95)	(0.04) - (0.65)	(-0.46) - (0.70)
median	-2.26	0.34	0.09
n =	(11)	(11)	(11)
7) range	(-3.01) - (-2.43)	(0.57) - (1.02)	(0.24) - (1.15)
median	-2.43	0.83	0.78
n =	(13)	(13)	(13)

atmosphere. Seasonal trends in log(PCO_2) values are discussed in Chapter Six.

It is interesting to note, although not unexpected when one considers the lithology of the catchment areas, that the three major surface streams and Spring Creek have negative median SI_{cal} and SI_{dol} values indicating undersaturation. Back Creek, Tara Creek and Scrubby Creek 4 are certainly different in that they have higher median log(PCO_2) values than the other four sites, and all three have positive median SI_{cal} and SI_{dol} values indicating supersaturation with respect to both calcite and dolomite.

For the Buchan and Murrindal Rivers the only occasion on which these sites were supersaturated with respect to either calcite and dolomite was in February 1983.

The Buchan River, Murrindal River, Spring Creek and Back Creek all recorded similar log(PCO_2), SI_{cal} and SI_{dol} values in July 1984 (−3.01 to −2.81, −2.28 to −2.01 and −4.81 to −4.26 respectively) with all except Spring Creek recording the lowest SI_{cal} and SI_{dol} values noted over the study period.

KARST SPRING AND CAVE WATER SITES

Median log(PCO_2) values range from −2.43 (New Guinea 2) to −1.44 (B-67) (Table 4.8), which are respectively ≈ 12 and 120 times normal atmospheric carbon dioxide level. All sites sampled in February 1983 were supersaturated with respect to calcite with all sites, except New Guinea 6, also being supersaturated with respect to dolomite.

TABLE 4.8. RESULTS OF COMPUTED PARAMETERS (LOG(PCO$_2$), SI$_{cal}$ and SI$_{dol}$) FOR KARST SPRING AND CAVE WATER SITES (SITES NUMBERS AS IN TABLE 3.1). RANGE AND MEDIANS GIVEN (n = NUMBER OF SAMPLES). LOG(PCO$_2$) AS ATMOSPHERES; SI$_{cal}$ AND SI$_{dol}$ DIMENSIONLESS.

SITE NO.		Log P(CO$_2$)	SI$_{cal}$	SI$_{dol}$
8)	range	(-2.83) - (-2.10)	(-1.10) - (0.47)	(-2.85) - (0.38
	median	**-2.43**	**-0.76**	**-2.08**
	n =	(7)	(7)	(7)
9)	range	(-3.40) - (-1.79)	(-1.68) - (0.15)	(-3.79) - (-0.27)
	median	**-2.34**	**-0.34**	**-1.45**
	n =	(7)	(7)	(7)
10)	range	(-2.68) - (-1.68)	(-1.32) - (0.83)	(-3.12) - (1.05)
	median	**-2.25**	**0.11**	**-0.37**
	n =	(29)	(29)	(29)
11)	range	(-2.91) - (-1.75)	(-0.88) - (1.07)	(-2.75) - (1.50)
	median	**-2.19**	**0.52**	**0.40**
	n =	(18)	(18)	(18)
12a)	range	(-2.54) - (-1.72)	(-0.50) - (0.99)	(-2.09) - (1.01)
	median	**-2.06**	**0.41**	**0.00**
	n =	(12)	(12)	(12)
12b)	range	(-2.52) - (-1.54)	(-0.96) - (1.03)	(-3.18) - (1.06)
	median	**-2.18**	**0.54**	**0.22**
	n =	(22)	(22)	(22)
12c)	range	(-2.84) - (-1.93)	(-0.96) - (1.13)	(-3.18) - (1.32)
	median	**-2.51**	**0.70**	**0.52**
	n =	(20)	(20)	(20)
13)	range	(-2.34) - (-1.37)	(0.04) - (1.09)	(-0.62) - (1.87)
	median	**-1.87**	**0.62**	**0.86**
	n =	(20)	(20)	(20)
14)	range	(-2.140 - (-1.05)	(-0.29) - (0.61)	(-1.16) - (0.70)
	median	**-1.54**	**0.23**	**-0.05**
	n =	(30)	(30)	(30)
15)	range	(-2.13) - (-1.75)	(-0.05) - (0.42)	(-0.64) - (0.31)
	median	**-1.92**	**0.19**	**-0.08**
	n =	(7)	(7)	(7)
16)	range	(-2.06) - (-1.18)	(-0.69) - (0.65)	(-2.04) - (0.83)
	median	**-1.44**	**0.27**	**0.11**
	n =	(22)	(22)	(22)
17)	range	(-1.62) - (-1.30)	(0.04) - (0.46)	(-0.37) - (0.47)
	median	**-1.48**	**0.27**	**0.15**
	n =	(13)	(13)	(13)

Of the sites that were sampled in July 1984 (high flow event) Moons, Dukes and B-67 recorded lowest log(PCO_2) values noted for these sites (all were undersaturated with respect to both calcite and dolomite), M-4 and Scrubby Creek 2 had log(PCO_2) values similar to their respective median value whereas Scrubby Creek 3 and Bitch of a Ditch recorded a value notably higher than its respective median value. All sites sampled in July 1984, with the exception of Dukes recorded lowest SI_{cal} and SI_{dol} values with Bitch of a Ditch being the only site that remained supersaturated with respect to calcite.

As noted previously in this Chapter (see discussion on <u>in-situ</u> and chemical results) particular sites in this group can be designated as having water of particular physical and chemical characteristics. The results presented in Table 4.8 reinforce this idea of different water types, and trends noted are -:

i) New Guinea 2 and 6: generally undersaturated with respect to both calcite and dolomite; generally lowest log(PCO_2) values of the karst spring sites sampled. Classified as TYPE 1 water.

ii) M-4 and Scrubby Creek 2: very similar median log(PCO_2) and SI_{cal} values; both sites only undersaturated with respect to both calcite and dolomite in July and September 1984. Classified as TYPE 2 water.

iii) Bitch of a Ditch: supersaturated with respect to calcite on all occasions, only undersaturated with respect to dolomite on one occasion (July 1984). Classified as TYPE 3 water.

iv) B-67 and B-41: very similar medians for all parameters; usually supersaturated with respect to calcite; supersaturated with respect to dolomite on 60%-70% of occasions; generally highest log(PCO_2) values. Classified as TYPE 4 water.

v) Degassing of CO_2 i.e. a decrease in the median log(PCO_2) value is noted is going from Scrubby Creek 1 -> Scrubby Creek 2 -> Scrubby Creek 3 -> Scrubby Creek 4; the increase in SI_{cal} and SI_{dol} median values is associated with the rate of degassing exceeding that of $CaCO_3$ precipitation (see Chapter Seven for further discussion).

vi) Results for Moons, Dukes and Scrooges Vault are similar to those noted for the chemical results, i.e. medians tend to lie between those for the four water types designated.

MISCELLANEOUS SITES

The results for this group of sites varied considerably as one would expect for such a variety of sites (Table 4.9), and as noted previously with the chemical results, values obtained are best discussed in the context in which the sites were sampled. Remembering that the number of water samples collected from all sites in this group is limited only tentative conclusions can be made.

Un-named Seep: Again notably different results from those noted for the two New Guinea sites. Median $\log(PCO_2)$ value ≈ 100 times atmospheric value as opposed to ≈ 12 times for the two New Guinea sites. Although median SI_{cal} indicates supersaturation with respect to calcite, this site was only supersaturated on three out of five occasions.

Un-named Creek: Undersaturated with respect to calcite only in July 1984; median $\log(PCO_2)$ similar to that noted for Scrubby Creek 3.

Butchers Creek: Typical of results expected from a surface stream draining from non-carbonate rocks, i.e. undersaturated with respect to calcite and dolomite; median $\log(PCO_2)$ value similar to that noted for the Murrindal River.

TABLE 4.9. RESULTS OF COMPUTED PARAMETERS (LOG(PCO$_2$), SI$_{cal}$ and SI$_{dol}$ FOR ALL MISCELLANEOUS SITES EXCEPT SITE 33 (SITES NUMBERS AS IN TABLE 3.1). RANGE AND MEDIANS GIVEN FOR SITES WHERE n (NUMBER OF SAMPLES) ≥ 4, OTHERWISE RANGE OR VALUE GIVEN. LOG(PCO$_2$) AS ATMOSPHERES; SI$_{cal}$ AND SI$_{dol}$ DIMENSIONLESS.

SITE NO.		Log P(CO$_2$)	SI$_c$	SI$_d$
18)	range	(-2.08) - (-1.33)	(-0.86) - (0.19)	(-2.08) - (0.00)
	median	**-1.54**	**0.07**	**-0.66**
	n =	(5)	(5)	(5)
19)	range	(-2.69) - (-1.93)	(-1.31) - (0.82)	(-3.90) - (0.62)
	median	**-2.46**	**0.45**	**-0.16**
	n =	(4)	(4)	(4)
20)	range	(-3.41) - (-2.58)	(-1.99) - (-0.58)	(-3.96) - (-1.24)
	median	**-2.68**	**-1.57**	**-3.09**
	n =	(4)	(4)	(4)
21)	range	(-2.67) - (-2.23)	(-1.28) - (0.20)	(-2.85) - (-0.02)
	median	**-2.37**	**-0.58**	**-1.48**
	n =	(5)	(5)	(5)
22a)	range	(-2.37) - (-1.90)	(-1.38) - (-0.79)	(-2.65) - (-1.53)
	n =	(2)	(2)	(2)
22b)	value	-1.66	0.17	-0.14
22c)	range	(-2.58) - (-1.99)	(-0.62) - (1.03)	(-1.52) - (0.50)
	median	**-2.20**	**0.75**	**1.01**
	n =	(4)	(4)	(4)
23)	range	(-2.33) - (-1.76)	(-0.22) - (0.06)	(-1.71) - (-0.90)
	n =	(2)	(2)	(2)
24)	range	(-2.91) - (-2.88)	(-1.82) - (-0.93)	(-3.78) - (-2.18)
	n =	(2)	(2)	(2)
25)	value	-3.10	-1.55	-3.40
26)	value	-2.62	0.45	-0.17
27)	value	-2.68	-0.64	-1.66
28)	value i)	-3.24	-1.10	-1.72
	value ii)	-3.14	-1.19	-1.41
29)	value	-3.35	-1.75	-3.26
30)	value	-2.44	-1.78	-3.96
31)	value	-2.14	-1.09	-3.69

TABLE 4.9 (CONT.)

32) range	(-2.19) - (-2.07)	(0.76) - (0.92)	(1.25) - (1.62)
n =	(2)	(2)	(2)

Sub-Aqua: Supersaturated with respect to calcite on one occasion; higher median $\log(PCO_2)$ than that noted for the Murrindal River.

Spring Creek Falls: Values typical of a surface flowing stream and within the range of values noted for Spring Creek.

Spring Creek Dukes: Very similar to values noted at Dukes.

Spring Creek Moons: Notably supersaturated with respect to calcite and dolomite and records highest median SI_{cal} and SI_{dol} values of all sites sampled.

Fairy Creek: Values typical of those found for Spring Creek under similar flow conditions.

For the remaining sites values obtained for all three parameters lie within the range of values noted for all other sites sampled.

CLUSTER ANALYSIS

As previously noted in this Chapter, the karst spring and cave water sites that have similar median values for physical, chemical and computed parameters were subjectively classified into groups of sites. A cluster analysis technique is used here to see if the above groupings, and assumptions behind the groupings are reasonable. Cluster analysis is used (using median parameter values) on the data set for all sites sampled, not just the karst spring and cave water sites, where n, the number of water samples collected, ≥ 4, to identify "clusters" (groups of sites), and to see if one can also identify physical and chemical controls on groundwater chemistry. The technique of cluster analysis is well documented. It is frequently used by ecologists in hierarchical classifications of vegetation (Mueller-Dombois and Ellenberg, 1974; Williams, 1976). It is an objective technique for detecting natural groupings in data; classifying sites into groups where neither the number of groups nor the members of the groups are known in advance.

An agglomerative polythetic classification was used on the data matrix in which all variables were standardised due to the differing scales of measurement, e.g. pH, water temperature, conductivity etc.. Standardised values were expressed as standard deviations around a mean of zero, i.e. z scores. The cluster analysis technique begins with each site assigned to a cluster with a single member and then agglomerates these clusters into a hierarchy of larger and larger clusters until finally a single cluster contains all sites.

The Cluster Module in PC SYSTAT was used to perform the classifications. A normalised euclidean distance matrix was calculated using the average linkage method for defining clusters and distances between clusters. Output is generated in the form of a dendogram (or tree diagram) in which dissimilarity increases as the number of clusters, or groups, decreases.

For the 23 sites selected (Table 4.10) 15 parameters were entered into the data matrix. The parameters were Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-}, alkalinity, total hardness, $\log(PCO_2)$, SI_{cal}, SI_{dol}, water temperature, pH, conductivity, Ca^{2+}/Mg^{2+} and Na^{+}/Cl^{-}. The resulting dendogram, is shown in Figure 4.2.

In Figure 4.2 it can be seen that the most "similar" sites are Dukes, B-67 and B-41, i.e. they are joined together in a cluster at the lowest level of dissimilarity. The next clusters to form are the two that contain Scrubby Creek 4 and Scrubby Creek 3, and Scrubby Creek 1 and Scrubby Creek 2, followed by a cluster

TABLE 4.10. SITES AND SITE NUMBERS USED IN CLUSTER ANALYSIS (SITES NUMBERS THE SAME AS IN TABLE 3.1).

SITE NUMBER	SITE NAME
1)	Buchan River
2)	Murrindal River
3)	Snowy River
4)	Spring Creek
5)	Back Creek
6)	Tara Creek
7)	Scrubby Creek 4
8)	New Guinea 2
9)	New Guinea 6
10)	Moons
11)	M-4
12a)	Scrubby Creek 1
12b)	Scrubby Creek 2
12c)	Scrubby Creek 3
13)	Bitch of a Ditch
14)	Dukes
15)	Scrooges Vault
16)	B-67
17)	B-41
18)	Un-named Seep
19)	Un-named Creek
20)	Butchers Creek
21)	Sub-Aqua

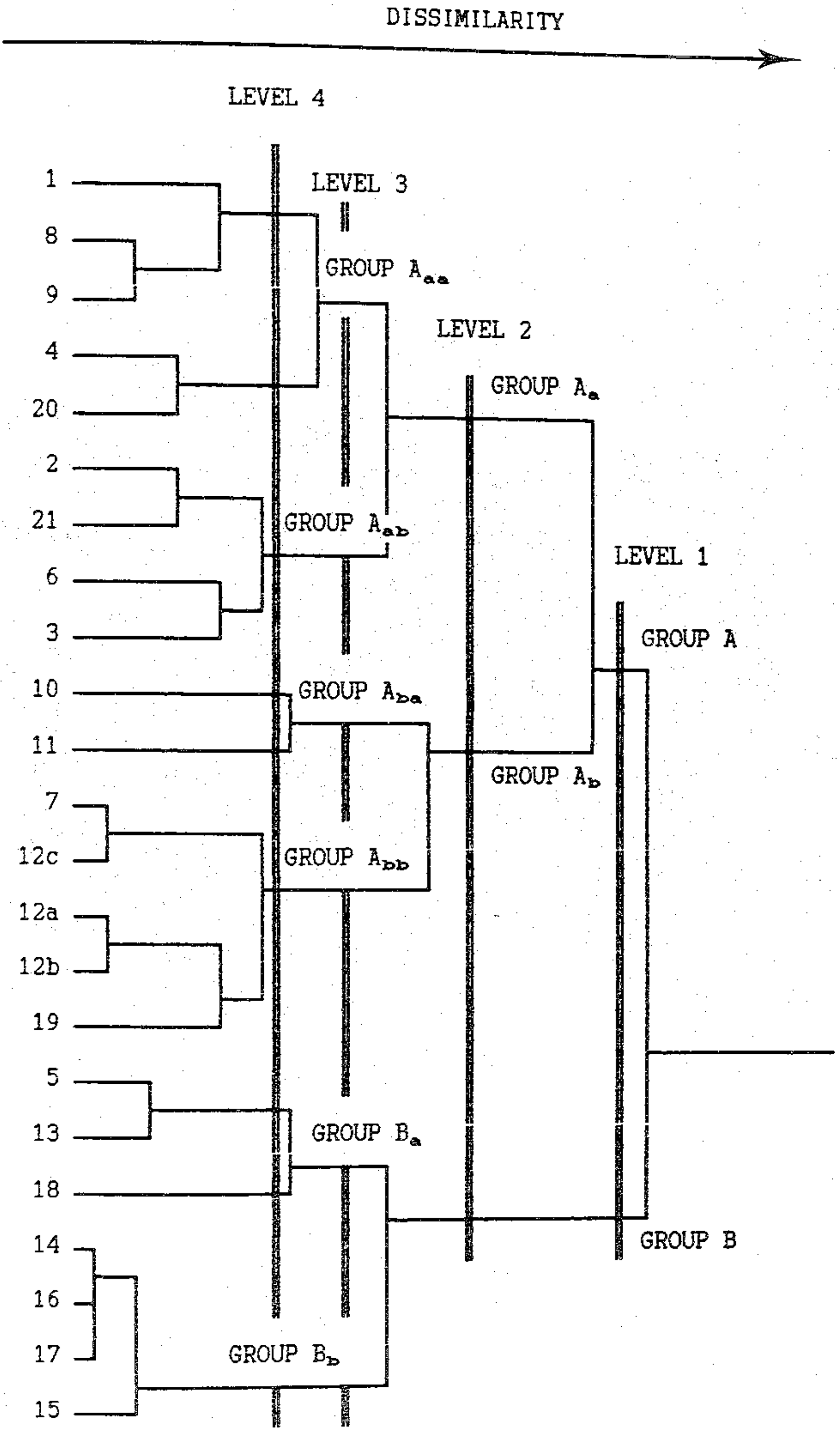


Figure 4.2. Dendogram derived by Cluster Analysis. (Site numbers as in Table 4.10).

containing New Guinea 2 and New Guinea 6. It can be seen then that at different levels of dissimilarity differing numbers of clusters occur, e.g. at level four, nine groups occur; at level three, six groups are evident and at levels two and one, three and two groups respectively.

It must be stressed here that these "levels" are chosen subjectively and do not represent a particular level of significance. The level at which one "looks at" the clusters is open to interpretation: one needs to ensure a sufficient summarisation of the data set, while at the same time retaining information about important differences between clusters of sites and it is this ordering of the sites that will now be looked at in more detail.

THE TWO GROUP LEVEL.

It can be seen from Figure 4.2 that two distinct groups of sites exist at this particular level of dissimilarity. Group A comprises sites 1, 2, 3, 4, 6, 7, 8, 9, 10, 11, 12a, 12b, 12c, 19, 20 and 21 which includes sites from all the categories listed at the start of this Chapter, i.e. major and minor surface stream sites, karst spring and cave water sites and miscellaneous sites. Likewise GROUP B (sites 5, 13, 14, 15, 16, 17 and 18) also includes sites from all categories. Recalling the four water TYPES proposed in the chemical results section of this Chapter for the karst spring and cave water sites, it is interesting to find that sites classified as having TYPE 1 or TYPE 2 water are in the GROUP A sites, whereas sites classified as having TYPE 3 or TYPE 4 water are clustered together in the GROUP B sites. Mean parameter values and standard deviations for the two groups of sites are given in Table 4.11.

It must be remembered that these values are the gross mean values at a particular level of dissimilarity. In broad terms, the GROUP B sites have a slightly higher mean water temperature, have notably higher mean cation and anions levels (hence higher mean conductivity and total hardness values), except for K^+, and are supersaturated with respect to both calcite and dolomite when compared to the GROUP A sites. The GROUP A sites have higher mean pH, Ca^{2+}/Mg^{2+} and $Na^+/Cl-$ values.

THE THREE GROUP LEVEL.

At this level of dissimilarity it can be seen that the GROUP A sites are subdivided into two groups (GROUP A_a and GROUP A_b) whereas the sites in GROUP B remain together. Mean parameter values and standard deviations for the three groups are given in Table 4.12. More subtle differences that exist between the sites in GROUP A (TWO GROUP LEVEL) become evident - GROUP A_a sites are lower in conductivity, mainly due to large differences in mean

TABLE 4.11. MEAN PARAMETER VALUES AND STANDARD DEVIATIONS FOR THE TWO GROUPS DEFINED BY CLUSTER ANALYSIS. ALL ION CONCENTRATIONS mg/l; ALKALINITY (ALK.) AND TOTAL HARDNESS (TOTHD.) AS mg/l $CaCO_3$; LOG(PCO_2) AS ATMOSPHERES; WATER TEMPERATURE (W_T.) AS °C; CONDUCTIVITY (COND.) AS µS cm^{-1} 25°C; Na^+/Cl^- AND Ca^{2+}/Mg^{2+} AS MOLAR RATIOS (EPM); SI_{cal} AND SI_{dol} DIMENSIONLESS.

	Ca^{2+}	Mg^{2+}	Na^+	K^+	Cl^-	Alk.	Tothd.	log(PCO_2)	SI_{cal}	SI_{dol}	W_T.	Na^+/Cl^-	Ca^{2+}/Mg^{2+}	Cond.	pH
GROUP A	53.4	8.3	17.0	2.3	31.3	154.9	167.8	-2.46	-0.22	-0.96	15.4	1.237	4.287	448	7.55
S.D.	37.5	3.5	7.3	0.9	15.2	91.6	98.3	0.26	0.80	1.30	1.6	0.170	3.361	218	0.24
GROUP B	131.9	33.2	59.9	2.6	163.6	351.1	467.1	-1.69	0.27	0.09	16.3	0.653	2.458	1181	7.24
S.D.	40.7	7.0	35.8	0.8	113.6	65.4	113.6	0.25	0.17	0.46	0.9	0.165	0.698	373	0.19

Ca^{2+} and alkalinity values when compared to the GROUP A_b values, these sites are also undersaturated with respect to both calcite and dolomite whereas the GROUP A_b sites are supersaturated with respect to both these minerals. Mean water temperature, Mg^{2+}, Na^+, Cl^- and Na^+/Cl^- molar ratio values are virtually the same between these two groups.

The GROUP A_a sites comprise predominantly surface stream sites (both major and minor) together with karst spring sites - New Guinea 2 and New Guinea 6 (TYPE 1 water sites). It is interesting to note that although Tara Creek (tributary stream) records median parameter values much closer to those sites in GROUP A_b it is clustered in with the GROUP A_a sites. The GROUP A_b sites (Scrubby Creek 1, 2, 3 and 4, Moons, M-4 and Un-named Creek) comprise predominantly karst spring sites, and as noted previously in this Chapter all except the Un-named Creek site were classified as being examples of TYPE 2 water.

THE SIX GROUP LEVEL.

This level is the most significant level at which to discuss the clustering of the sites due to the "individuality" of the groups. At lower levels of dissimilarity individual sites start to appear as individual groups. Particular groupings of sites, in

TABLE 4.12. MEAN PARAMETER VALUES AND STANDARD DEVIATIONS FOR THE THREE GROUPS DEFINED BY CLUSTER ANALYSIS. ALL ION CONCENTRATIONS mg/l; ALKALINITY (ALK.) AND TOTAL HARDNESS (TOTHD.) AS mg/l $CaCO_3$; LOG(PCO_2) AS ATMOSPHERES; WATER TEMPERATURE (W_T.) AS °C; CONDUCTIVITY (COND.) AS $\mu S\ cm^{-1}$ 25°C; Na^+/Cl^- AND Ca^{2+}/Mg^{2+} AS MOLAR RATIOS (EPM); SI_{cal} AND SI_{dol} DIMENSIONLESS.

	Ca^{2+}	Mg^{2+}	Na^+	K^+	Cl^-	Alk.	Tothd.	log(PCO_2)	SI_{cal}	SI_{dol}	W_T.	Na^+/Cl^-	Ca^{2+}/Mg^{2+}	Cond.	pH
GROUP A_a	25.1	7.6	17.7	2.6	31.2	87.4	95.7	-2.58	-0.78	-1.86	15.4	0.895	2.054	300	7.48
S.D.	22.2	3.4	9.5	1.0	19.3	59.3	63.7	0.25	0.58	0.97	2.1	0.186	1.213	65	0.17
GROUP A_b	89.8	9.2	16.1	1.8	31.5	241.7	260.5	-2.30	0.51	0.20	15.4	0.835	7.205	581	7.68
S.D.	10.7	3.6	3.4	0.7	8.9	25.9	30.0	0.17	0.23	0.40	1.0	0.159	2.911	65	0.22
GROUP B	131.9	33.2	59.9	2.6	163.6	351.1	467.1	-1.69	0.27	0.09	16.3	0.653	2.458	1181	7.24
S.D.	40.7	7.0	35.8	0.8	113.6	65.4	113.6	0.25	0.17	0.46	0.9	0.165	0.698	373	0.19

particular GROUP B_b (Dukes, Scrooges Vault, B-67 and B-41) and GROUP A_{bb} (Scrubby Creek 1, 2, 3 and 4 and the Un-named Creek site) are not that unexpected as these groups represent sites that have been previously classified as being TYPE 4 and TYPE 2 water respectively. Mean parameter values and standard deviations are given in Table 4.13 for the six groups of sites.

GROUP A_{aa}. Buchan River, Spring Creek, New Guinea 2 and 6 and Butchers Creek: - This grouping is quite surprising in that the two New Guinea karst spring sites are clustered in this group, in particular with the Buchan River. The other two surface stream sites in this group (Spring and Butchers Creeks) are quite similar in respect to the majority of median values noted for New Guinea 2 and 6. In fact Butchers Creek, as noted previously in Chapter Three, receives runoff from the opposite side of the ridge where New Guinea 2 and 6 are located. Notably lower mean Ca^{2+}, alkalinity, total hardness, SI_{cal}, SI_{dol} and water temperature values than those observed for the respective GROUP A_{ab} parameters.

GROUP A_{ab}. Murrindal River, Snowy River, Tara Creek and Sub-Aqua:- Sub-Aqua is as noted in Chapter Three a cave entrance through which, depending upon flow conditions existing in the Murrindal River, all or part of the flow re-emerges, and hence its grouping at least with the Murrindal River is not surprising. The inclusion

TABLE 4.13. MEAN PARAMETER VALUES AND STANDARD DEVIATIONS FOR THE SIX GROUPS DEFINED BY CLUSTER ANALYSIS. ALL ION CONCENTRATIONS mg/l; ALKALINITY (ALK.) AND TOTAL HARDNESS (TOTHD.) AS mg/l $CaCO_3$; LOG(PCO_2) AS ATMOSPHERES.; WATER TEMPERATURE (W_T.) AS °C; CONDUCTIVITY (COND.) AS $\mu S\ cm^{-1}$ 25°C; Na^+/Cl^- AND Ca^{2+}/Mg^{2+} AS MOLAR RATIOS (EPM); SI_{cal} AND SI_{dol} DIMENSIONLESS.

	Ca^{2+}	Mg^{2+}	Na^+	K^+	Cl^-	Alk.	Tothd.	log(PCO_2)	SI_{cal}	SI_{dol}	W_T.	Na^+/Cl^-	Ca^{2+}/Mg^{2+}	Cond.	pH
GROUP A_{aa}	17.3	6.4	15.3	2.9	27.9	65.3	71.5	-2.60	-1.02	-2.37	13.8	0.972	1.958	252	7.41
S.D.	9.1	3.9	8.1	1.2	21.0	29.0	30.8	0.23	0.49	0.73	0.6	0.217	1.282	95	0.09
GROUP A_{aa}	34.8	9.1	20.6	2.3	35.3	115.0	126.0	-2.57	-0.48	-1.22	17.4	0.799	2.174	361	7.54
S.D.	31.2	2.2	11.6	0.8	19.1	80.1	85.9	0.32	0.58	0.91	1.1	0.086	1.303	228	0.20
GROUP A_{ba}	86.2	14.4	19.3	2.7	39.0	245.3	270.4	-2.22	0.32	0.02	14.3	0.764	3.638	633	7.52
S.D.	18.0	0.4	3.4	0.1	2.8	51.3	47.2	0.04	0.29	0.54	1.1	0.074	1.155	81	0.15
GROUP A_{bb}	91.2	7.2	14.9	1.4	28.5	240.2	256.6	-2.33	0.59	0.27	15.9	0.863	8.632	560	7.75
S.D.	9.1	1.4	2.7	0.2	8.8	18.4	27.0	0.20	0.18	0.38	0.5	0.182	1.862	53	0.22
GROUP B_a	97.1	33.0	25.7	1.8	51.9	350.0	382.0	-1.83	0.31	0.17	15.7	0.818	1.838	848	7.32
S.D.	26.8	6.7	6.0	0.3	19.0	57.3	68.8	0.27	0.28	0.77	1.3	0.100	0.590	96	0.22
GROUP B_b	158.1	33.4	85.6	3.2	247.4	352.0	531.0	-1.60	0.24	0.03	16.7	0.530	2.924	1430	7.12
S.D.	26.6	8.3	22.4	0.2	60.9	79.7	99.8	0.22	0.04	0.11	0.3	0.024	0.262	281	0.11

of Tara Creek in this cluster is certainly surprising in that for the majority of parameters the median values at this site are certainly much higher than those recorded at the other sites in this cluster. Tara Creek appears to be clustered in this group due to its high median water temperature (18.0°C) and high pH value (7.63).

GROUP A_{ba}. Moons and M-4:- M-4 has usually been more closely associated with Scrubby Creek 2 and 3. The main differences between this group and GROUP A_{bb} are the higher mean Mg^{2+} and K^{+} values (almost double) noted, as well as a lower mean water temperature and Ca^{2+}/Mg^{2+} value.

GROUP A_{bb}. Scrubby Creek 1, 2, 3 and 4 and Un-named Creek:- It would have been more surprising if these sites had not been clustered together. As noted in Chapter Three (site descriptions) the four Scrubby Creek sites represent four different locations along the same system, i.e. cave water, spring outlet, ≈65m downstream of the spring outlet and ≈50m further downstream. The Un-named Creek site when it does flow, channels water underground which is presumed to connect into the Scrubby Creek cave and spring system where the other four sites in this group are located. Highest mean Ca^{2+}/Mg^{2+} molar ratio of all the GROUP A sub-groups which is a lithology related factor.

GROUP B_a. Back Creek, Bitch of a Ditch and Un-named Seep:- Bitch of a Ditch had been assumed to be in a class by itself and the clustering with two other sites is surprising, although when one looks at the physical and chemical evidence the grouping of these three sites makes more sense. Back Creek is located close to where Bitch of a Ditch is located and hence the chemical effect due to both sites having catchments predominantly of dolomite mostly likely explains the clustering of these two sites. Also the physical evidence suggests that Back Creek is fed by diffuse flow. The Un-named Seep site is located in the same outlier of Buchan Caves Limestone as New Guinea 2 and 6, and the physical and chemical results obtained are certainly different from those noted at the two New Guinea sites.

GROUP B_b. Dukes, Scrooges Vault, B-67 and B-41:- As noted for GROUP A_{bb}, if these sites had not been clustered together it would have been surprising. Main differences between the two B GROUP's are that for this group, i) higher mean Ca^{2+}, Na^+, K^+, Cl^-, total hardness, Ca^{2+}/Mg^{2+} and water temperature values are noted, and ii) lower mean pH and Na^+/Cl^- values are noted.

THE NINE GROUP LEVEL.

At this level of dissimilarity it can be seen (Figure 4.2) that individual sites, e.g. Moons, M-4 and the Un-named Seep site, are "clustered " as individual groups, with two of the other groups consisting of only two sites. It would seem then that the groups defined at the six group level allow a better overall discussion of the "groups" rather than at this particular level in which, for some cases, individual site characteristics are being discussed.

Overall then it can be seen that the cluster analysis technique is a useful tool for clustering sites with particular characteristics together. The level of dissimilarity at which the clusters of sites are looked at is fairly subjective, and in the cluster analysis of the data collected in this study, the six group level was decided upon as it provided the best summarisation of the data set.

Comparing the karst spring and cave water sites which had previously been classified by chemical characteristics into 4 water TYPES it is interesting to note that the cluster analysis technique, at the SIX GROUP LEVEL, clusters these sites into 5 groups.

PROPOSED GROUPINGS	CLUSTERED GROUPINGS
TYPE 1 WATER - SITES 8 AND 9	GROUP A_{aa} - SITES 8 AND 9
TYPE 2 WATER - SITES 10, 11, 12a, 12b AND 12c	GROUP A_{ba} - SITES 10 AND 11 GROUP A_{bb} - SITES 12a, 12b AND 12c

TYPE 3 WATER - SITE 13	GROUP B_a - SITE 13
TYPE 4 WATER - SITES 14, 15, 16 AND 17	GROUP B_b - SITES 14, 15, 16 AND 17

It can be seen then the only real difference between the above groupings is that the TYPE 2 water sites have been split into two groups. At the THREE GROUP LEVEL, as noted previously, it is interesting to note that all of these sites are grouped together. Hence the groupings proposed are justified by the results of the cluster analysis technique.

SUMMARY

In this Chapter the results obtained from, i) *in-situ* field measurements, ii) chemical analyses, and iii) the computer speciation program have been presented for a variety of sites that were sampled during the study period. Based mainly on differences in median chemical values the karst spring and cave water sites were subjectively classified into groups of sites having water of one of the four proposed TYPES. Cluster analysis also reinforced the idea of, at least four different water types existing for the karst spring and cave water sites. Other sites that were sampled during the study, in particular the minor surface streams which have catchments of predominantly carbonate rocks, were also classified into the different groups noted above. The spatial variation of the physical, chemical and computed characteristics of the karst spring and cave water sites, as well as some of the other sites sampled, will be examined in the following Chapter.

CHAPTER FIVE

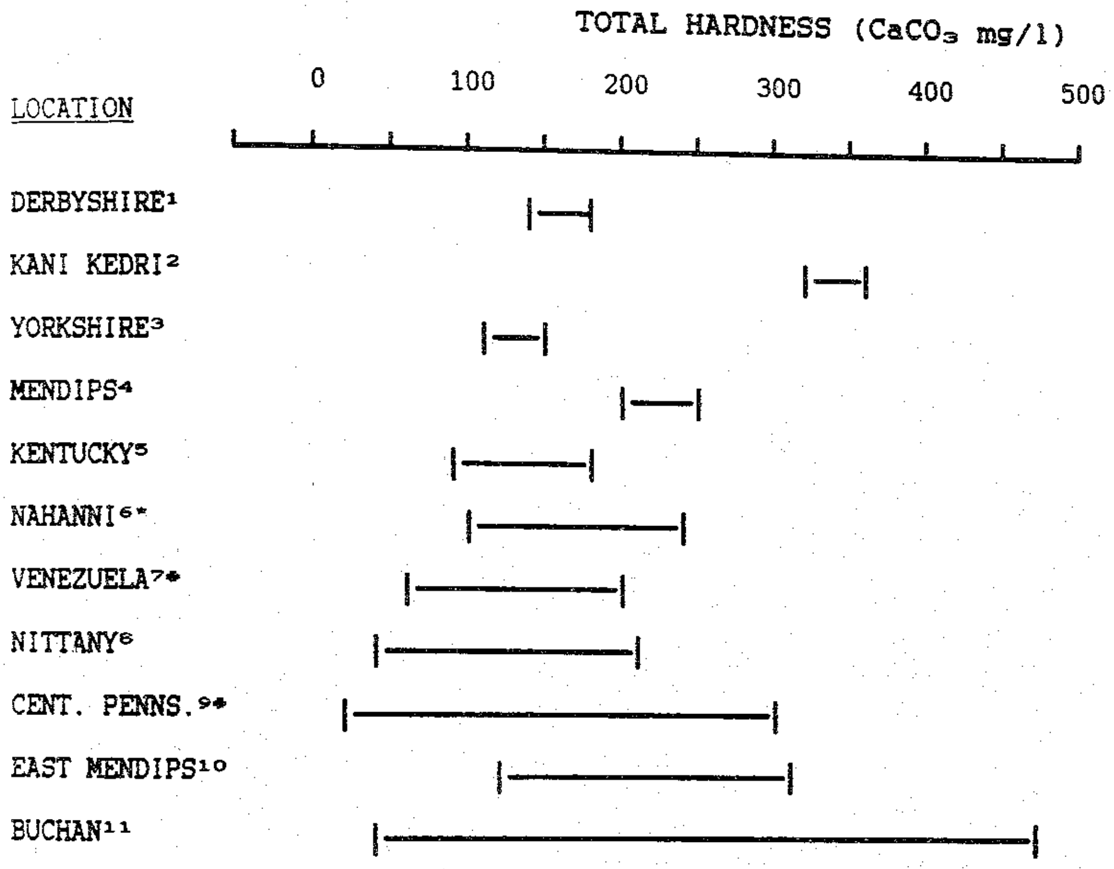
SPATIAL VARIABILITY

In the previous Chapter it was shown that the karst spring and cave water sites could be divided into groups on the basis of physical and chemical characteristics of the water sampled. In this Chapter the spatial distribution of measured and computed parameters will be examined and reasons proposed for the spatial variability noted.

INTRODUCTION

In theory, for a homogeneous and stratigraphically uniform carbonate terrain, the physical and chemical characteristics of spring waters discharging from such an area would be expected to show little spatial variation in parameters measured, e.g. total hardness.

In Figure 5.1 the range of mean total hardness values, for spring waters **only**, from various carbonate locations are shown together with the range of median total hardness values for the karst springs sampled in this study. It should be noted that the ranges of values given, unless otherwise noted, are ranges of mean values, which for some locations include springs discharging both allogenic and autogenic recharge while other springs may only discharge autogenic recharge.



[1] Christopher, 1980; [2] Jawad and Hussien, 1986; [3] Cooper and Pitty, 1977; [4] Atkinson, 1977b; [5] Harmon and Hess, 1982; [6] Brook and Ford, 1982; [7] Gascoyne, 1974; [8] Shuster and White, 1971; [9] Langmuir, 1971a; [10] Drew, 1970; [11] This Study.

Figure 5.1. Range of mean total hardness values for spring waters from various locations (as mg/l $CaCO_3$). Buchan data median values. * Grouped spring water data, ◆ range of single values only.

It can be seen then that in reality, for some carbonate terrains, e.g. Derbyshire, Kani Kedri and Yorkshire, the spatial variation in mean total hardness is small. For other carbonate terrains the spatial variation in total hardness values tends to be more diversified, and a range of ≈ 1 to 4 times the lowest mean spring value is not uncommon. It can also be seen that the Buchan spring water data (median total hardness) shows considerably more spatial variation than that found in other parts of the world and possible explanations for this variation will now be examined.

SPATIAL VARIATION OF BUCHAN SPRING WATER CHARACTERISTICS

The median values of selected parameters for the karst springs examined in this study are given in Table 5.1 together with the respective data for a number of other sites. Data for the other sites are included for a number of reasons, i) the four cave water sites are included as they represent "limestone groundwater" rather than "karst spring water" and also because water from two of these sites is known to discharge at two of the karst springs; ii) Back Creek and Tara Creek are included because they are surface streams draining catchments of predominantly dolomite and predominantly Taravale Formation respectively; iii) The Un-named Seep site is included because of its proximity to two of the karst spring sites (New Guinea 2 and New Guinea 6); and iv) Butchers Creek is included as the median chemical values obtained at this site best represents water draining from Snowy River Volcanics, and hence can represent "background" chemical levels, i.e. water with no carbonate rock contact.

Spatially, the karst spring water sites show a wide

TABLE 5.1. MEDIAN VALUES OF SELECTED PARAMETERS FOR KARST SPRING WATER (SITES 8 TO 14), CAVE WATER (SITES 12a, 15, 16 AND 17) AND THREE SURFACE STREAM SITES (SITES 5, 6 AND 20). Ca^{2+} AND Cl^- AS mg/l; Ca^{2+}/Mg^{2+} AND Na^+/Cl^- AS MOLAR RATIOS (EPM); LOG(PCO_2) AS ATMOSPHERES; SI_{cal} DIMENSIONLESS AND W_T = WATER TEMPERATURE °C.

SITE NO.	Ca^{2+}	Cl^-	Ca^{2+}/Mg^{2+}	Na^+/Cl^-	Log(PCO_2)	SI_{cal}	W_T
KARST SPRING SITES							
8	25.3	19.5	3.44	1.03	−2.43	−0.76	14.0
9	27.1	19.2	3.21	1.10	−2.34	−0.34	13.5
10	73.5	41.0	2.82	0.82	−2.25	0.11	13.5
11	98.9	37.0	4.45	0.71	−2.19	0.52	15.0
12b	97.8	33.0	8.08	0.77	−2.18	0.54	16.0
13	121.2	61.2	2.01	0.74	−1.87	0.62	17.0
14	157.8	211.0	2.99	0.55	−1.54	0.23	16.9
CAVE WATER SITES							
12a	102.7	31.1	9.65	0.81	−2.06	0.41	16.0
15	120.5	180.5	3.27	0.49	−1.92	0.19	16.5
16	177.6	300.2	2.73	0.54	−1.44	0.27	17.0
17	176.4	297.8	2.71	0.54	−1.48	0.27	16.5
SURFACE STREAM SITES							
5	68.2	64.4	1.18	0.78	−2.07	0.24	15.5
6	80.0	62.1	3.98	0.93	−2.26	0.34	18.0
20	8.9	29.8	0.84	0.75	−2.68	−1.57	13.8

variation in median values for all parameters, and this is most noticeable when a comparison is made between the data obtained for New Guinea 2 and Dukes. Median Ca^{2+}, Mg^{2+}, Na^+ and total hardness values are ≈ 6 times higher at Dukes than the respective median values noted for New

Guinea 2, with median Cl− values being ≈ 11 times higher. The median CO_2 value for Dukes is ≈ 8 times the median value for New Guinea 2 (2.88% compared with 0.37%). It is interesting to note that although median chemical values differ quite markedly between these two sites, the respective median Ca^{2+}/Mg^{2+} molar ratios are not that dissimilar which possibly reflects the control of catchment lithology on spring water composition. Other controls such as the residence time of water and soil CO_2 levels are also quite important and may in fact overshadow the effect of catchment lithology on spring water chemistry.

SPATIAL VARIATIONS IN CALCIUM AND MAGNESIUM AND Ca^{2+}/Mg^{2+} MOLAR RATIOS

Ca^{2+}/Mg^{2+} molar ratio values have been used extensively in groundwater studies to delineate the lithological control on groundwater flowing through either limestone or dolomite or mixed carbonate aquifers. Ca^{2+}/Mg^{2+} molar ratios of ≈ 1.0 are taken to indicate groundwater flow through predominantly dolomite bedrock (Hsu, 1963; Douglas, 1965; Meisler and Becher, 1967; Shuster and White, 1972; White, 1988), with molar ratios in the range 3.0–10.0 or greater indicating flow through limestone and molar ratios of 1.5–3.0 generally indicating flow in a mixed dolomite-limestone aquifer.

For spring waters discharging from carbonate aquifers both Douglas (1965) and White (1988) stress the point that low Ca^{2+}/Mg^{2+} molar ratios do not necessarily imply flow through dolomite bedrock or a mixed carbonate bedrock sequence but could simply be due to the enrichment of Mg^{2+}, in terms of molar proportions, by the loss of Ca^{2+} from solution by calcite precipitation.

Catchment lithology, i.e. the chemical composition of the rock types within a particular spring's catchment and the percentage contribution of these rock types within the catchment boundary, at least for the springs at Buchan, is perceived to have an important effect on spring water composition. For instance, as noted in Chapter Three, although all springs occur only in Buchan Caves Limestone the proportions of carbonate and non-carbonate rocks within a particular spring's catchment area can vary considerably. Also to be taken into account is the fact that the carbonate group as a whole varies (group comprises three different carbonate units), as well as the fact that the chemical composition of the Buchan Caves Limestone unit varies considerably ranging from 52.9% $CaCO_3$ and 43.5% $MgCO_3$ (dolomite) to 95.6% $CaCO_3$ and 0.2% $MgCO_3$ (limestone) (Jenkin and Baxter, 1968).

Using the data set assembled by Jenkin and Baxter (1968) for the chemical composition of the Buchan Caves

Limestone unit (n=79), Ca^{2+}/Mg^{2+} molar ratios range from 1.69 (dolomite) to 663.9 (limestone). It must be stressed that these molar ratios would only be obtained in solution if congruent dissolution is assumed, i.e. the entire solid dissolves, and there is no external input of Ca^{2+} or Mg^{2+} into the system or loss of these ions from the system. An average composition of this unit gives a Ca^{2+}/Mg^{2+} value of 7.84.

For all the karst springs at Buchan, except one (Bitch of a Ditch), water discharging at the spring can be physically traced varying distances back into cave systems with all of these systems being "active", i.e. they are actively depositing calcite speleothems such as flowstone, stalagmites, etc. Hence when looking at the median Ca^{2+}/Mg^{2+} values obtained, some Ca^{2+} ions, depending on flow regimes etc., may have already been lost from the system, i.e. precipitated out as $CaCO_3$. Median molar ratio values obtained would then be lower than those expected if after dissolution no loss of Ca^{2+} occurs.

For example comparing the results obtained in Chapter Four for the four Scrubby Creek sites (1, 2, 3 and 4) although median Mg^{2+} values are ≈ the same for all four sites, median Ca^{2+} values differ and the median molar ratio decreases in going from the cave (9.65) to the spring (8.08) to the end of the tufa terraces (7.24) to ≈ 50m downstream (6.85). Hence for the karst springs at Buchan these molar ratios give a rough indication of catchment lithology. It must be remembered that the above limitations can apply especially when the water emerging at the spring is in effect a "mixture of waters" that have taken a variety of pathways through the system.

For each site sampled, particularly those draining carbonate lithologies, field observations on the predominant catchment lithology were made in order to assess median Ca^{2+}/Mg^{2+} values obtained. For the Buchan Caves Limestone member, dolomite was distinguished from limestone by either the surface weathering features (see Chapter One) and/or by the use of dilute hydrochloric acid. Murrindal Limestone was distinguished from Buchan Caves Limestone by the use of geological information (Teichert and Talent, 1958; Jenkin and Baxter, 1968). It was felt that despite the obvious limitations in delineating carbonate rocks on the above criteria, the methods used were, at a broad scale, reasonably accurate.

The spatial distribution of median Ca^{2+}/Mg^{2+} molar ratios are shown in Figure 5.2 for the karst spring sites as well as for other sites sampled that have the majority of their catchment in the study area and where $n \geq 4$.

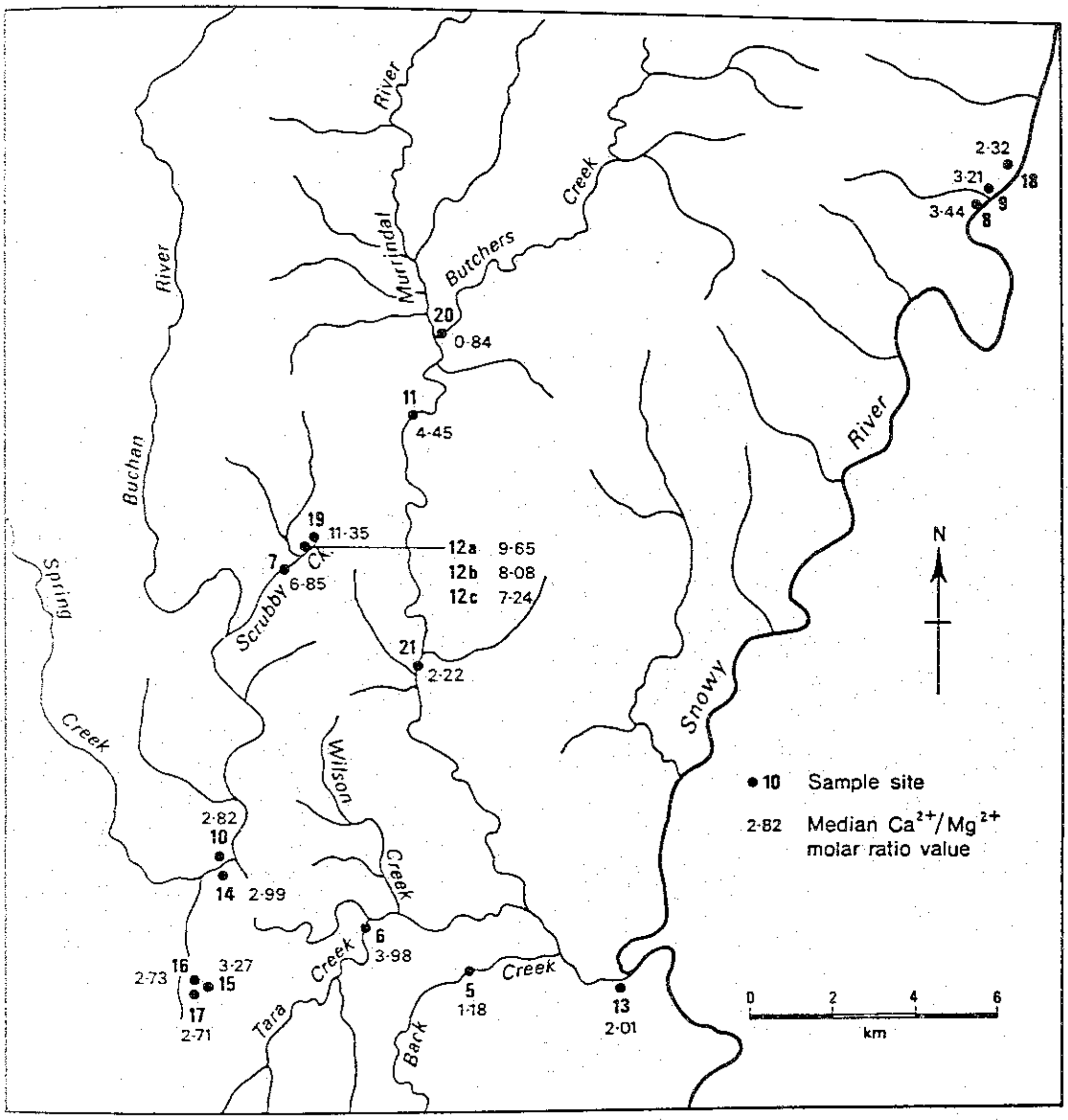


Figure 5.2. Spatial distribution of median Ca^{2+}/Mg^{2+} molar ratios. Site numbers as per Table 3.1.

Back Creek has the lowest median Ca^{2+}/Mg^{2+} molar ratio (1.18) of all sites and this is consistent with this site having a large proportion of dolomite outcropping in its catchment. For the karst spring sites, Bitch of a Ditch has the lowest median Ca^{2+}/Mg^{2+} molar ratio (2.01) with this site having the highest proportion of dolomite in its catchment for the karst spring and cave water sites. Scrubby Creek 2, for the karst spring water sites, has the highest median Ca^{2+}/Mg^{2+} molar ratio (8.08) and is consistent with this site having virtually all limestone in its catchment. As noted previously, Scrubby Creek 1 (cave water site) has a molar ratio of 9.65. The Un-named Creek site (an intermittent surface stream) located close to the Scrubby Creek sites has a median Ca^{2+}/Mg^{2+} molar ratio of 11.4. This value is assumed to be representative of surface runoff in this part of the study area before it is channelled underground. For the other karst spring water sites median Ca^{2+}/Mg^{2+} molar ratios range between the two values given above.

It can be seen that in the southern half of Figure 5.2 all sites, excluding Scrooges Vault and Tara Creek, record molar ratios indicating dolomite or a mixed dolomite-limestone type aquifer, if Ca^{2+}/Mg^{2+} molar ratios of ≈ 1.0 and ≈ 1.5-3.0 are taken to infer the respective type of aquifer. Tara Creek has a catchment of predominantly calcareous mudstone (Taravale Formation) which may explain its relatively high molar ratio. The difference noted in median molar ratios between B-67 and B-41 (2.73 and 2.71 respectively) and that of Scrooges Vault (3.27) is quite noticeable. Possible reasons for this difference will be proposed when the spatial variation in median Cl^- values are discussed. The central sites, excepting Sub-Aqua, record the highest molar ratios and indicate either, a lack of the basal part of the Buchan Caves Limestone (dolomite) or the influence of the high purity Murrindal Limestone. Based on field evidence it would appear to be a combination of both (see also Figure 2.3). The lower median molar ratio noted at Sub-Aqua (2.22 compared with 4.46-9.65 for the other sites in this area) is attributed to be simply due to the dilution of limestone groundwater (e.g. M-4) with water draining from non-carbonate rocks (e.g. Butchers Creek).

For the New Guinea Ridge sites the molar ratio at the Un-named Seep site (2.32) indicates a mixed type of aquifer, while the ratios for New Guinea 2 and New Guinea 6 (3.44 and 3.21) possibly indicate a limestone aquifer. The difference between these sites is possibly a reflection of residence time rather than a lithological factor. Flow through times are quite critical if equilibrium with respect to either dolomite or limestone is achieved; White (1988) notes that a year or more may be necessary for water in contact with dolomite to reach equilibrium, whereas water in contact with limestone for ≈ 10 days can reach equilibrium. This is examined in more detail when median SI_{cal} and SI_{dol} values are discussed.

The influence of the contribution of Ca^{2+} and Mg^{2+} ions from non-carbonate rock types within a particular karst springs catchment to the concentration of ions found where the spring discharges is not easily calculated. This is due to the fact that most of the runoff from the non-carbonate rocks generally percolates into the soil profile developed, albeit a shallow system, and is not easily traced before it disappears on reaching the limestones and dolomites in the study area.

There are no readily accessible straightforward examples of small surface streams draining from the surrounding non-carbonate rocks, disappearing underground on reaching the limestone and reappearing some distance away at one of the spring outlets so that the inputs from non-carbonate sources can be calculated. Runoff from the Snowy River Volcanics is assumed to have physical and chemical characteristics similar to those noted for Butchers Creek. It is interesting to note that Butchers Creek receives runoff from the opposite side of the ridge in which New Guinea 2, New Guinea 6 and the Un-named Seep site are located and has a median Ca^{2+}/Mg^{2+} molar ratio of 0.84 with a catchment of non-carbonate rocks.

Of the karst spring sites examined it is obvious that for New Guinea 2 and New Guinea 6 (lowest median Ca^{2+} and Mg^{2+} values) any contribution of these ions in solution from the surrounding Snowy River Volcanics will be of a greater influence than the contribution of these ions to the median values noted at any of the other karst spring sites. If the median Ca^{2+} value for Butchers Creek is taken to representative of water draining Snowy River

Volcanics, it represents ≈ 30% of the median value for New Guinea 2 and 6 and ≈ 7–12% of the medians for the other karst spring sites that have Snowy River Volcanics in their catchments.

B-67 and B-41 record the highest median Ca^{2+} and Mg^{2+} values noted at any of the sites sampled in this study. Whether these respective median values are really representative of uncontaminated groundwater or not is discussed further when the spatial variation of median Cl^- values is examined.

Input of Ca^{2+} and Mg^{2+} ions from atmospheric sources are assumed to be of minor importance given the results in Chapter Four, and would appear to have very little, if any, affect on the overall chemical composition observed at any of the karst spring sites and would certainly contribute nothing to the observed spatial variation.

SPATIAL VARIATION IN CHLORIDE AND Na^+/Cl^- MOLAR RATIOS

Median Na^+ and Cl^- values vary considerably over the study area ranging from 13.4 and 19.2 mg/l respectively at New Guinea 6 to 104.2 and 300.2 mg/l respectively at B-67 (factors of ≈ 8 and ≈ 15 times respectively). Catchment lithology would appear to play little, if any role at all in explaining the significant spatial variation noted, as both the above sites are located in

Buchan Caves Limestone.

To obtain a clearer picture of possible causes or effects that may explain the spatial distribution noted, median Cl− and Na+/Cl− molar ratios for selected sites are shown in Figure 5.3. (A molar ratio of 0.86 is assumed to indicate a straightforward recycling of atmospheric NaCl derived from seawater - molar ratios of Na+/Cl− in two rainwater samples at Buchan were found to be 0.91 and 1.01 respectively, indicating a molar excess of Na+ ion concentration over molar Cl− ion concentration).

From Figure 5.3 it is interesting to note, i) the highest median Cl− values (also the lowest median Na+/Cl− molar ratios) are associated with the four sites located in the southwestern corner of the study area (B-67, B-41, Dukes and Scrooges Vault) and would appear to be quite localised; ii) four sites with different catchment lithologies (Spring Creek, Back Creek, Tara Creek and Bitch of a Ditch) and located in the southern part of the study area all record similar median Cl− values ranging from 61.2 mg/l to 64.4 mg/l. Three of these sites (Spring Creek, Back Creek and Bitch of a Ditch) also record very similar median Na+/Cl− molar ratios (0.74-0.78); and, iii) for the remaining sites, sites that are located at the bottom of discharge areas (e.g. Moons, Butchers Creek and Scrubby Creek 2) record median chloride values

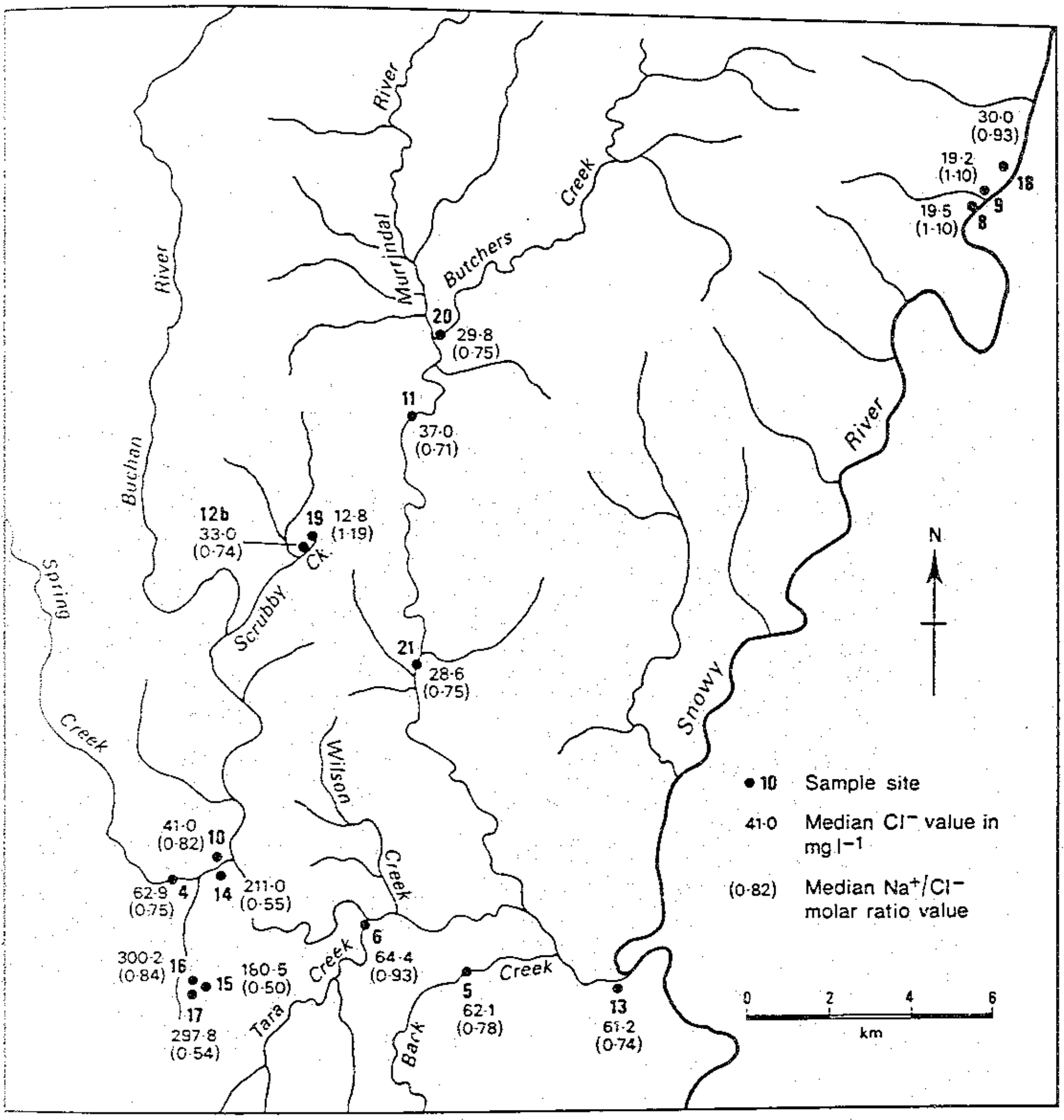


Figure 5.3. Spatial distribution of median Cl^- and median Na^+/Cl^- molar ratio values. Site numbers as per Table 3.1.

ranging from 28.6 mg/l (Sub-Aqua) to 41.0 mg/l (Moons) and molar ratios < 0.86. Sites that are located at a relatively high elevation in a particular catchment or are completely covered by native vegetation have median Cl^-'s ranging from 12.8 mg/l (Un-named Creek) to 30.0 mg/l (Un-named Seep site). These sites also recorded the highest molar ratios (0.93 to 1.19).

B-67, B-41, DUKES AND SCROOGES VAULT

These four sites certainly stand out from the rest of the sites sampled because of the quite high median Na^+ and Cl^- (also Ca^{2+}) concentrations found at these sites, in particular B-67 and B-41 (Table 5.1). As noted previously three of these four sites are located close together (B-67, B-41 and Scrooges Vault) with the fourth site (Dukes) having been connected to B-67 by fluorescent dye tracing (a straight line distance of approximately 2.5km with a flow time of 24 days (flow rate of 0.12 cm/sec) under "normal" flow conditions, i.e. discharge at Dukes is ≈ 4l/s).

The higher median Na^+ and Cl^- values noted at these four sites when compared to the median values noted at the other sites sampled are not easily explained but high positive correlations of Na^+ with Cl^- values (all significant at the 99% level; r = 0.915 (B-41), 0.96 (Dukes), 0.97 (B-67) and 0.995 (Scrooges Vault)) indicate a close relationship between these two ions.

One possible source of this high Na^+ - Cl^- water could be the Tertiary sands and gravels that are located just to the south of three of these sites (B-67, B-41 and Scrooges Vault, Figure 5.4). As these gravels are of fluvial and not marine origin, they would appear not to be the source area and spot sampling showed this to be the case. Spot water samples were collected from, a) two

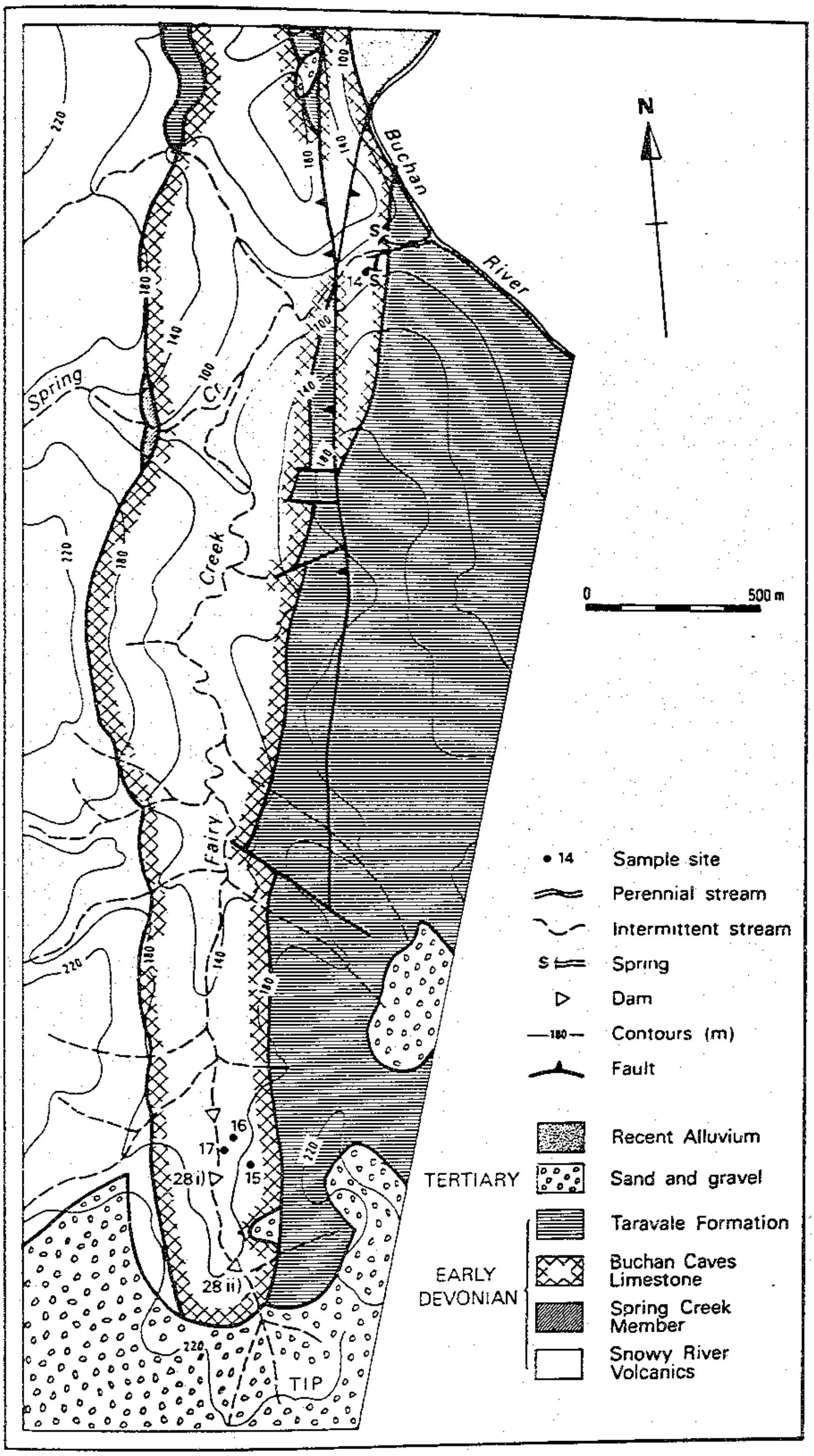


Figure 5.4. Map showing the location of the tip in relationship to sample sites 14, 15, 16, 17, 28i) and 28 ii). Geological boundaries also shown. Site numbers as per Table 3.1.

farm dams (sites 28 i) and ii)), one located 400m downslope from the refuse dump (tip) and the other about 200m further downslope, b) a minor stream draining southwards from the sands and gravels (site 30; Figure 3.2), and c) a borehole (site 29; Figure 3.2) located approximately 1km south of the refuse dump, in an attempt to locate the origin of this high Na^+ - Cl^- water. The range of Na^+ and Cl^- values obtained were 16.4-29.8mg/l and 14.0-52.9mg/l respectively, which are notably lower than the median values recorded at any of the four above sites which tended to prove that the gravels and sands were not the source.

Another source could be that leachate from the refuse dump, located in the sands and gravels about 700m upslope from B-67, B-41 and Scrooges Vault, infiltrates into, and contaminates the groundwater (Figure 5.4).

Cases of groundwater contamination by leachate from refuse sites have been reported in the literature world-wide (Qasim and Burchinal, 1970; Agpar and Langmuir, 1971; Kimel and Braids, 1974; Zenone et al, 1975; Kunkle and Shade, 1976; Murray et al, 1981; Das and Kidwai, 1983; Knight, 1983; Shug and Young, 1987; Mulvey et al, 1987; Knight and Beck, 1987). The contribution of contaminants, both organic and inorganic, to a groundwater system is extremely diversified and depends upon a myriad of considerations, e.g. type or types of refuse being dumped, whether it is solid or liquid, whether or not it is compacted, whether or not a landfill site is effectively lined, etc. As this aspect is beyond the scope of this study readers are referred to Lu et al (1985) for further references and discussion.

The inorganic chemical composition of leachate is, as noted above, extremely diverse. For instance, Fungaroli (1971, in Lu et al, 1985) quotes ranges of constituents from 50–2,400mg/l Cl^-, 100–4,000mg/l Na^+ and 300–6,000mg/l total hardness in leachate; Johansen and Carlson (1976) in their study of leachate from landfill sites in both Norway and America reported Ca^{2+}, Mg^{2+}, Na^+ and Cl^- concentrations ranging from 99–400mg/l, 13–96mg/l, 35–462mg/l and 68–680mg/l respectively; Zenone et al (1975) in their study of leachate from three disposal sites in Alaska reported dissolved constituents ranging from 2 to 20 times greater than levels found in the surrounding unaffected groundwater.

Chloride because of its conservative nature has been used quite extensively as a tracer to delineate inputs and outputs in leachate, recharge and groundwater movement studies (Agpar and Langmuir, 1971; Peck, 1983; Mather et al, 1983; Sharma, 1987; Mazor, 1987; Johnston, 1987a, 1987b; Macpherson and Peck, 1987; Williamson et al, 1987; Reynolds and Pomeroy, 1988). For example Agpar and Langmuir (1971) in their study of leachate from a sanitary landfill noted of the species in the leachate, chloride was most readily leached from the refuse and since it is virtually unaffected by reactions in the soil, i.e. ion exchange processes, it passed straight into the groundwater system. Therefore because of chloride's conservative nature, the median Cl− values found at Spring Creek (62.9mg/l), Back Creek (64.4mg/l), Tara Creek (62.1mg/l) and Bitch of a Ditch (61.2mg/l) are assumed to represent background Cl− levels for this, predominantly cleared, southern part of the study area. Hence median Cl−'s at Scrooges Vault, Dukes, B-67 and B-41 are ≈ 2 to 4 times background levels, with the refuse dump appearing to be the most obvious source of this contamination.

As noted above, spot water samples were collected from two farm dams which are located directly downslope from the refuse dump. Based on the results of the chemical analyses of water from these two sites it appears that leachate by-passes these two sites. For example Cl− values were 30.9mg/l and 52.9mg/l respectively which are notably lower than the respective medians at B-67, B-41 and Scrooges Vault. It is hypothesised that leachate from the refuse dump infiltrates relatively quickly through the sands and gravels where it is located until it reaches the underlying limestone where it mixes in with the limestone groundwater.

As noted previously (Chapter Four) the highest median Ca^{2+}, Mg^{2+} and Na^{+} values found in this study are also associated with groundwater at B-67 and B-41. If, as assumed above, the high Cl^{-} values found are due to contamination by leachate, and given the possible ranges of ion concentrations found in leachate for these ions (see above), it would appear likely then that the high Ca^{2+}, Mg^{2+} and Na^{+} noted at B-67 and B-41 could also be due to contamination and are not, as assumed in Chapter Four, representative of "limestone" groundwaters in this part of the study area.

The lower median Ca^{2+}, Mg^{2+}, Na^{+}, HCO_3^{-} and Cl^{-} values noted at Dukes when compared to the respective medians noted at B-67 (and B-41) are assumed to be simply due to the mixing of water from B-67 with water or waters derived further down in the catchment. This is examined in more detail in Chapter Six.

The lower median ion concentrations noted at Scrooges Vault when compared to the respective medians at B-67 (and B-41) are harder to explain particularly when one considers the relative closeness of these three sites. (Median ion values at Scrooges Vault are ≈ 68%, ≈ 57%, ≈ 55%, ≈ 58% and ≈ 60% of the respective median Ca^{2+}, Mg^{2+}, Na^{+}, HCO_3^{-} and Cl^{-} values at B-67). As noted in Chapter Four groundwater movement at this site has been extremely hard to determine and perhaps even though all three sites are located close together, groundwater at Scrooges Vault does represent a different groundwater body than that found at B-67 and B-41. Given that the "groundwater level" or "water table" (assuming one does exist in limestone areas) is at the same height for all three sites this would appear unlikely. Where the leachate from the refuse dump first mixes with the "limestone groundwater" and its preferred flow path need to be resolved before the this can be fully addressed.

One effect of the high Cl^- values noted is that more Ca^{2+}, and possibly Mg^{2+}, ions could be released into the groundwater than that predicted by equilibrium reactions because of increased dissolution of carbonate bedrock due to the ionic strength effect (Back and Hanshaw, 1970; Long and Saleem, 1974; see also Chapter One). Drever (1982) showed that general charge balance equation for carbonate waters (ignoring minor species) could be written as,

$$\underbrace{m_{Na+} + m_{K+} + 2m_{Mg2+} - m_{Cl-} - 2m_{SO4-}}_{M} + 2m_{Ca2+} = m_{HCO3-} + 2m_{CO3-}$$

and that if the expression for M was negative more carbonate dissolution could take place. Median M values for the karst spring and cave water sites are,

New Guinea 2 -: 0.545
New Guinea 6 -: 0.518
Moons -: 0.487
M-4 -: 0.949

Scrubby Creek 1 -: 0.448

Scrubby Creek 2 -: 0.248

Bitch of a Ditch -: 2.700

Dukes -: 0.008

Scrooges Vault -: -0.584

B-67 -: -0.544

B-41 -: -0.281

hence it can be seen that, for at least B-67, B-41 and Scrooges Vault, increased dissolution can take place.

It can be seen then that for these four sites a more detailed water sampling programme, including a number of groundwater bores at specific locations, is needed to, i) fully resolve the effect of the leachate on groundwaters in this part of the catchment, and ii) to elucidate groundwater movement and mixing processes.

ALL OTHER SITES

The spatial variation in median Cl- values shown in Figure 5.3 for all sites, except for the four sites discussed above, is assumed to be primarily related to whether or not a particular sites catchment has been cleared and converted to pasture rather than catchment lithology. Sites with the higher median Cl- values, e.g. Back Creek and Spring Creek drain catchments that have a large proportion of their catchment cleared of native vegetation and are used predominantly for cattle or sheep grazing. These two sites are also located at the "bottom" of their respective discharge areas, i.e they are the end points of their respective catchments.

Increases in Cl- levels in ground and stream waters following the conversion of land covered by native vegetation to crop and pasture production are reported quite extensively in the literature (Peck, 1983; Anon., 1987; Johnston, 1987c; Peck and Williamson, 1987; Williamson et al, 1987; Borg et al, 1988; Schofield and Ruprecht, 1989). The increase in Cl- values is attributed to an increase in salt storage in the soil profile due to a decrease in precipitation interception and transpiration following clearing which results in a rise in the water table. Soluble salts bought in by precipitation are concentrated in the soil by evapotranspiration and are easily transported to shallow groundwater aquifers and surface streams when they are flushed from the soil profile (Figure 5.5).

Johnston (1987a, 1987b, 1987c) found what he termed "salt bulges" (shown in Figure 5.5) in a number of soil cores examined in his study of the distribution of chloride and its relationship to subsurface hydrology after the clearing of native vegetation (i.e. the mechanisms of water flow and recharge to groundwater). He found that although salt was distributed vertically within the profile the maximum salt concentrations occurred as a salt bulge in the unsaturated zone and much lower salt concentrations were observed in the saturated zone (Johnson, 1987c). It must be remembered that no where in the present study area would the depth of soil development noted by Johnston exist, and that the "salt bulge", if on does exist, would be closer to the surface compared to that at ≈ 5m depth noted by Johnston. Williamson et al (1987) in their study of the same five catchments Johnston used in his studies, estimated that the equilibration time for a new salt balance following clearing ranged from 30 to 200 years.

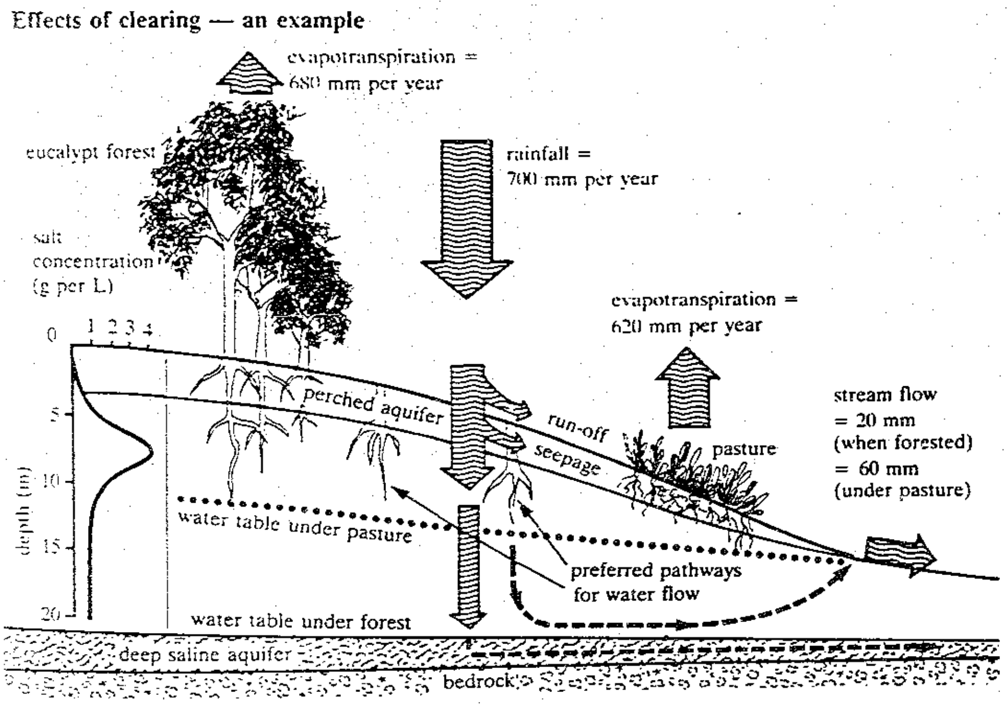


Figure 5.5. Clearing reduces evapotranspiration, so more water reaches the water table. This rises, carrying salt into the stream. (After Bell, 1988/89).

Schofield and Ruprecht (1989) in their study on the regional analysis of stream salinisation in Western Australia found that although chloride concentrations increased in stream and ground waters (hence salinisation) following clearing, annual total rainfall played an important role in determining in how quickly this increase took place. They found that soil salt storage was strongly correlated with annual total rainfall, i.e. catchments with lower annual rainfall totals (<900mm yr^{-1}) which had been cleared, recorded over a 20 year period, a rapid increase in stream salinities.

Hence although it has been proposed that the spatial distribution of median Cl^{-}'s noted in this study is mainly attributed to the clearing of native vegetation, the strong rainfall gradient that exists across the study area (818mm yr^{-1} at Buchan township to ≈ 1500mm yr^{-1} at New Guinea Ridge) will obviously be important in determining recharge and flushing rates. As noted for the four sites assumed to be affected by groundwater contamination, a much more detailed sampling and monitoring programme is needed before deciding whether clearing is more important than annual rainfall.

SPATIAL VARIATIONS IN MEDIAN LOG(PCO_2), SI_{cal} AND SI_{dol} VALUES

Median log(PCO_2) values for the karst spring sites (Table 5.1) ranged from −2.43 (New Guinea 2) to −1.54 (Dukes) indicating theoretical equilibrium with an atmosphere containing 0.37% and 2.88% CO_2 respectively. Overall, median $\log(PCO_2)$ values ranged from −2.68 (Butchers Creek, ≈ 0.21% CO_2) to −1.44 (B-67, ≈ 3.63% CO_2) which are respectively ≈ 7 and ≈ 120 times normal atmospheric CO_2 level. The spatial distribution of median $\log(PCO_2)$ values for selected sites are shown in Figure 5.5.

The spatial variations noted in median $\log(PCO_2)$ values are assumed to be mainly related to the residence time of recharge with catchment lithology and vegetation cover playing minor roles. Sites that are assumed to have fast flow through times for recharge have little chance for equilibrium to be established between "recharge" and bedrock (see discussion earlier in this Chapter). This is most evident for the three New Guinea Ridge sites.

The area where all three sites are located is covered in native vegetation and as such soil PCO_2 levels are assumed to be the same, catchment lithology is also assumed to be similar. Recharge for New Guinea 2 and New Guinea 6 is assumed to move through the system relative quickly in comparison to water emerging at the seep site with this being reflected in the median $\log(PCO_2)$ and in particular the SI_{cal} values noted at these sites. As noted by Drake and Wigley (1975, p.959), "The saturation index tells how far the water has evolved towards equilibrium and is therefore dependent on residence time

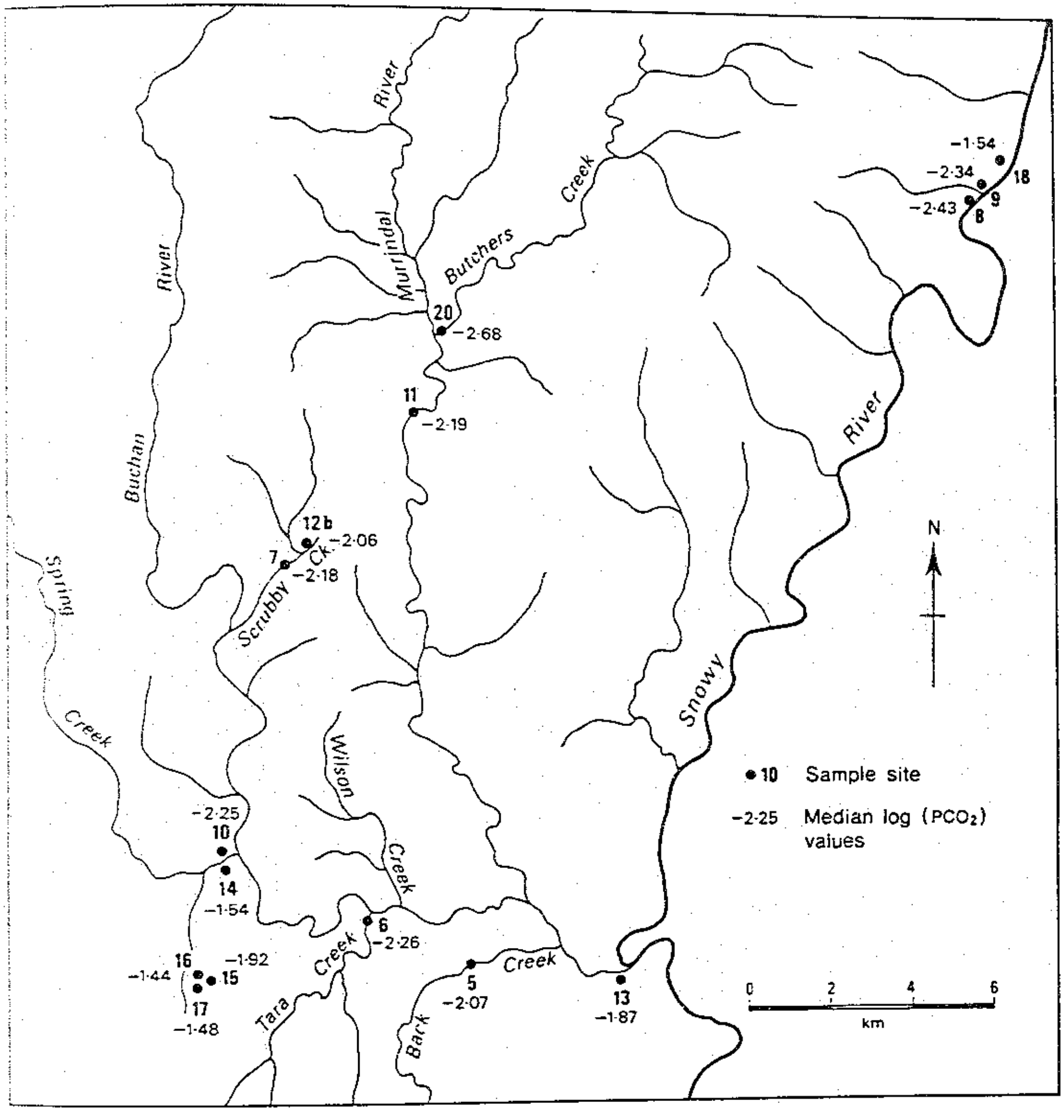


Figure 5.6. Spatial distribution of median log(PCO_2) values. Site numbers as per Table 3.1.

in the aquifer". Furthermore SI_{cal} values have often been used to distinguish between conduit flow (fast flow through times) and diffuse flow (long residence times) systems (White, 1969; Shuster and White, 1972; Drake and Wigley, 1975). This classification of flow types is looked at in more detail when the response over time of the sites sampled (temporal variability) is examined in Chapter Six.

New Guinea 2 and 6 are both undersaturated with respect to calcite (and dolomite) and record median CO_2 values that are ≈ 11 and ≈ 14 times atmospheric CO_2 level (compared with ≈ 7 times for Butchers Creek). For the seep site, median SI_{cal} value indicates water just supersaturated with respect to calcite (0.07) and a theoretical CO_2 level ≈ 100 times higher that of normal atmosphere.

All other karst spring sites, as well as the cave water sites and Back and Tara Creek record positive median SI_{cal} values indicating supersaturation with respect to calcite with all of these sites also recording larger median $\log(PCO_2)$ values than New Guinea 2 and 6. Of these sites all, except Moons and Dukes, are either at equilibrium (Scrubby Creek 1) or are supersaturated with respect to dolomite.

Unfortunately no soil or cave carbon dioxide levels were measured during this study, but cave CO_2 levels ranging from 0.05% (Moons Cave, median value of 30 cave air samples collected between 10.3.1985 and 21.8.1985) to 0.074% (Lilli Pilli Cave, median value of 36 cave air samples collected between 6.3.1985 and 17.8.1985) to spot values of approximately 3.0% to 4.0% (M-100 and Stirlings Cave - Potholes area, Figure 2.6) have been reported from the Buchan area (Canning, 1985; Ackroyd, 1987; 1988; 1989). When expressed as $\log(PCO_2)$ values a range from-

3.30 to −1.40 is obtained. The log(PCO_2) value of −1.40 is very similar to the median values noted at B-67 and B-41. Canning (1985) also gives a value of 0.21% for a soil CO_2 value found near Lilli Pilli Cave.

SPATIAL VARIATION IN MEDIAN WATER TEMPERATURE

Based on the assumption that groundwater temperature approximates mean annual air temperature (MAT; Drake, 1980) and using air temperature data that is available for the two closest meteorological stations to the study area (Orbost and Nowa Nowa, Figure 2.1), groundwater temperatures would be expected to be around 14.0–14.4°C. It is interesting therefore that for the karst spring and cave water sites, seven out of the eleven sites (Table 5.1) are notably warmer (median water temperature values from 16.0°C to 17.0°C) than MAT and four sites are close to, or are slightly cooler (median water temperature from 13.5°C to 15.0°C) than MAT. (Median water temperature values for the Buchan and Snowy Rivers (using all available R.W.C data, Table 4.1) are 14.8°C and 15.0°C respectively).

One reason for this discrepancy noted could be the way that MAT is calculated. As noted in Chapter Two no air temperature data are available for Buchan but air temperature data are available for Orbost (1938–1989) and Nowa Nowa (1948–1956 and 1965–1975). MAT for each station was calculated as the average of the sum of mean monthly minimum and mean monthly maximum air temperature and was 14.4°C for Orbost and 14.0°C for Nowa Nowa.

Jennings (1979a; 1983) in his studies of the Blue Waterholes noted an appreciable difference between spring water temperature (10.8°C - Cliff Foot Rising) and MAT (7.4°C). Two possible reasons were suggested for this discrepancy (Jennings, 1979a), i) soil temperatures were higher than air temperatures (this would affect percolation water temperature), and ii) as most of the drainage goes underground it escaped the effect that cold air pondage over the Plain had on surface streams. Based on the mean temperature of drip waters (10.8°C) in Murray Cave (close to the surface), Jennings accepted the first explanation.

Crowther (1982) noted a cooling rather than a warming effect in his study of the thermal characteristics of seepage waters in four Malaysian Caves. He found that average seepage water temperatures were 2 to 3°C cooler than MAT. Soil temperatures, on slopes with native vegetation, he noted were ≈ 2°C lower than MAT and that this effect as well as the fact that cave air temperatures were also lower (no direct insolation) contributed to the discrepancy between seepage water temperatures and MAT.

Shimano (1988) in a study of over 300 spring water sites in and around the Aso caldera found that spring water temperatures were ≈ 2.0°C higher than MAT. This discrepancy was considered to be due to either, i) a rise in recharge water temperature by its passage underground, or ii) higher recharge rates occurring during the warmer early summer to autumn period, with a answer yet to be resolved.

Assuming that groundwater temperature approximates MAT another factor could be that the sites where the warmer water temperatures are noted have catchments that have little or no native vegetation cover due to either clearing, or because large areas of rock outcrop exist. These sites also mainly have a north to north-west slope aspect and that these areas act as heat source for percolating waters.

Another factor could be that catchment elevation plays an important role in determining groundwater temperatures, i.e. the higher the catchment the lower the groundwater temperature. For example, Shimano (1988) found an inverse relationship between spring water temperature and altitude where,

$$Tw = -0.00641H + 18.17 \quad (n > 300,\ r = 0.694)$$

Tw = spring water temperature and H = altitude in metres.

No soil temperature data were collected in this study but for the cave water sites that were sampled, cave air temperature measurements were also taken at the point of water sampling. Quite notably B-67, B-41 and Scrooges Vault all recorded median cave air temperatures of 17.0°C. For Scrubby Creek 1 the median cave air temperature was 16.5°C. Hence it can be seen that at least for these sites, if MAT is around 14.0 to 14.4°C, some source of heat transfer is taking place.

In Figure 5.7 median water temperatures (and standard deviations) for the karst spring and cave water sites are shown. For the karst spring and cave water sites, leaving out Moons for the moment, median water temperature values decrease as one proceeds northwards, i.e. the sites sampled in the southern part of the study area tend to be warmer. The exception to this "trend" is Moons, which is very similar in water temperature to that for New Guinea 2 and 6, also of interest is that the actual spring outlets for Moons and Dukes are only ≈ 70m apart on opposite sides of Spring Creek yet median water temperatures differ by 3.4°C.

There is no clear relationship in the data between water temperature and elevation as all of the karst spring and cave water sites occur below the 300m contour (Figure 5.7). However the two karst springs located at New Guinea Ridge have catchments >600m in elevation, which are the highest spring catchments in the area. In

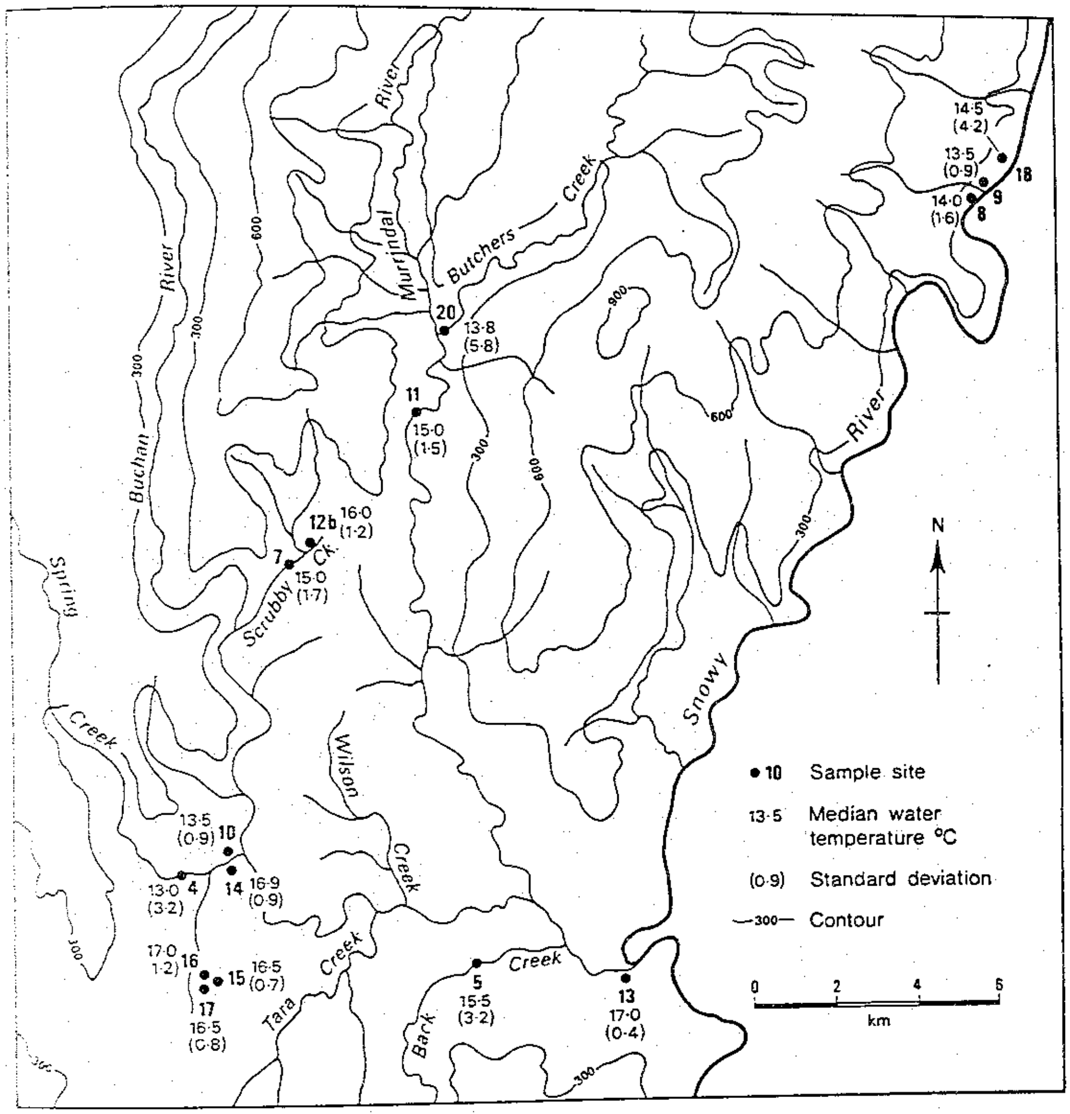


Figure 5.7. Spatial distribution of median water temperature values with standard deviations given in brackets.

the case of Moons median water temperature and standard deviation are exactly the same as for New Guinea 2 which tends to preclude elevation as having an effect on water temperature. It is felt that elevation plays a minimal role, if any, in determining karst spring and cave water temperatures.

The median water temperatures for two minor tributary streams also reinforce the idea of the importance of slope aspect and vegetation cover. Spring Creek (median water temperature of 13.0°C) drains a catchment that is predominantly forested and has mainly a southerly aspect whereas Back Creek (15.5°C) drains a catchment that has been mainly cleared of native vegetation and has a northerly slope aspect.

How recharge is transmitted through a particular karst springs catchment and its role in influencing spring water temperature is discussed in the next Chapter when temporal variability is examined.

SUMMARY

For the karst spring and cave water sites it has been shown that the median values for particular physical, chemical and computed parameters vary considerably over this small karst area and in some cases, e.g. Ca^{2+}, virtually span the range of Ca^{2+} values quoted in the literature for karst areas with temperate climates (see Smith and Atkinson, 1976; Ford and Drake, 1982).

Catchment lithology, vegetation cover (native or pasture), the residence time of recharge and slope aspect all play important roles, if not the major role, in explaining the spatial variability noted for particular individual parameters.

For some parameters this spatial distribution is easily explained while for others the spatial distribution is more difficult to explain. For example, the spatial distribution of the Ca^{2+}/Mg^{2+} molar ratio appears to be very much controlled by catchment lithology while the actual concentrations of Ca^{2+} and Mg^{2+} ions in solution, although dependent to a certain extent upon lithology, may well be determined by flow rates which in turn determine whether or not equilibrium is established between bedrock and the water passing through.

The spatial variability noted in this study for particular parameters such as Ca^{2+} and karst spring water temperature show that some caution must be exercised in "characterising" a particular karst area in terms of "average" parameter values selected to evaluate climatic control theories for landscape development in karst areas.

CHAPTER SIX

TEMPORAL VARIABILITY

In the previous Chapter it was shown that the median value of particular physical, chemical and computed parameters of the sites sampled varied considerably over the study area. This spatial distribution provides no information regarding the long or short term behaviour of, in particular, the karst spring waters.

In this Chapter the at-a-site variability of selected parameters, mainly for the karst spring and cave water sites, will be examined although data for some of the other sites sampled will also be included for comparative purposes.

The role of discharge, residence time and seasonality in explaining some or all of the variability noted will also be examined.

INTRODUCTION

In Chapter Four, for the presentation of the results the median value of the parameters examined was used in preference to the mean, or the average, because of the way in which the mean is biased by extreme values. For in-site variability, if the median value is used, the semi-interquartile range (SIQ, defined as $(Q_{75} - Q_{25})/2$, where Q_{75} and Q_{25} are the 75th and 25th percentile points respectively) provides some information concerning the variability of a data set. According to King (1969, p.26), "The basic problem with this measure (the SIQ) is that it ignores many of the values obtained and focuses attention only upon a specific value. The standard deviation takes into account all values within a particular data set and gives an indication of distribution about the mean". The standard deviation is alright for individual parameters at individual sites but generally precludes comparison between different parameters (differing units of measurement), and also between sites having significantly different mean values.

In a number of studies on karst waters, the co-efficient of variation of a particular parameter (e.g. total hardness, calcium hardness or spring water temperature) has been used as an indicator of variability for a particular site, and for comparing data from different sites. The co-efficient of variation is defined as the ratio of the standard deviation to the mean and is usually expressed as a percentage,
where C_v (%) = $(\sigma/\bar{x})100$, σ and $\bar{x}$ are the standard deviation and mean respectively.

Pitty (1966) in his study of seepage, pool and cave stream waters in Poole's Cavern examined calcium hardness variability; C_v's of calcium hardness ranged from 3.19%

(standing cave water) to 23.56% (stream water where it first re-emerges in the cave). C_v's of seepage waters ranged from 4.93% to 13.19%. He notes that the value of 23.56% was very similar to that recorded for surface streams in the same general area (14.07% to 25.19%) and attributed the high degree of variability to the varying supply of water from allogenic sources. The seepage sites he considered were all percolating water sites.

Paterson (1971) records C_v's of calcium hardness ranging from 1.0% to 4.7% for 10 Berkshire springs, and notes that the small C_v's of the spring waters were probably an indication of the slow circulation of water within the saturated zone.

Shuster and White (1971) proposed a method of distinguishing between conduit flow and diffuse flow springs on the basis of the C_v of total hardness (note not the C_v of calcium hardness). They found that sites exhibiting diffuse flow behaviour had C_v's of total hardness < 5.0%, and sites exhibiting conduit behaviour had C_v's between 10.0% and 24.0%. Shuster and White (1972) using the data presented in their 1971 paper found that C_v's of total hardness around 10.0% were probably a more reliable cut-off point for diffuse flow. They carefully noted that this classification was not a definitive one, i.e. some sites that exhibit diffuse flow behaviour (based on field evidence - lack of conduits, etc.) may have C_v's > 10.0%. For the data from 14 Central Appalachian springs, C_v's of total hardness ranged from 0.96% to 10.23% for the diffuse flow springs, with C_v's of 9.1% to 24.0% for the more variable conduit flow springs. They also noted that conduit flow spring waters were undersaturated with respect to both calcite and dolomite and that the high degree of variability noted at these sites was a reflection of variation in recharge, fast flow-through times and slow kinetics of equilibrium between water and rock.

In a study of limestone springs in the Central Pennines, Ternan (1972) found that the temporal variation in calcium hardness of the springs examined was highly correlated with flow-through times and a distinction could be made between allogenic karst waters and diffuse percolation systems by using the C_v of calcium hardness. Allogenic systems were associated with high calcium hardness variability (mean C_v of 13.5%) and rapid flow-through times, while a lower degree of calcium hardness variation (mean C_v 5.8%, range 2.2–10.6%) and longer flow-through times characterised diffuse systems. Using the data from 41 springs Ternan found that the relationship between the C_v of calcium hardness and flow-through time could be described by the equation, $\log C_v = 1.543 - 0.524 \log T$, ($r = 0.84$ and T = time in days), and concludes that (p. 320), "In addition to providing information on recharge to the limestone aquifers, the co-efficient of variation of calcium hardness provides an index of the residence time of circulating groundwater in these aquifers, which in turn may be related to factors such as degree of permeability, conduit development or the distance to the major recharge centres".

Newson (1972) and Ede (1972) both noted the applicability of the Shuster and White classification; Ede notes (p.54), "The categories used by Shuster and White may be considered the end-points of a continuum into which many springs fit. It is important that these end-points be clearly defined so that work can proceed on the recognition of the intermediate stages".

Cooper and Pitty (1977) in their study of 6 Yorkshire risings recorded C_v's of calcium hardness ranging from 16.49% to 19.74% with the C_v's of spring water temperatures ranging from 17.34% to 33.29%. Using the data of Cowell and Ford (1980; 1983) the C_v of Ca^{2+} ion concentration for conduit springs was 24.0% and 14.0% for diffuse springs. Although Atkinson (1977b) recorded C_v's of total hardness from 2.4% to 3.1% for 3 Mendip springs which suggested that the springs belonged to the diffuse flow category of Shuster and White (1971), he noted that, on hydrogeological evidence (Atkinson, 1977a), 60-80% of the spring flow was through conduits, although 80% of the recharge to the aquifer was by percolating water.

Thrailkill and Robl (1981) in their study of vadose waters in 3 Kentucky caves recorded C_v's of Ca^{2+} ion concentration ranging from 21-35% for vadose flow, 3-7% for low-Ca vadose seepage and 5-24% for high-Ca vadose seepage. Johnson (1981) in his study of The Sinking Valley Resurgence Complex recorded C_v's of total hardness ranging from 15.3% to 24.5% for conduit systems and C_v's of total hardness from 8.1% to 13.0% for diffuse flow springs. Halliwell (1981) in his study of the geohydrology of the Ingleborough area classified the risings into 5 groups based on mean $CaCO_3$ values and variability (C_v of calcium hardness). Mean C_v's for the first 3 groups were 40.2%, 25.0% and 18.7% respectively, with the two other groups being divided into >10% and <10.0% groups.

Jawad and Hussien (1986) recorded C_v's of total hardness ranging from 11.4% to 13.8% for 6 springs in northern Iraq. They noted that although these values were slightly higher than those proposed by Shuster and White (1971) and tended to indicate conduit rather than diffuse flow, they considered (based on the relationship between discharge response time to rainfall rather than the C_v of total hardness) the springs were of a diffuse flow nature.

Scanlon and Thrailkill (1987) recorded C_v's of total hardness for major springs (10-17%) and high level springs (11–17%) and although physically the major springs corresponded to conduit springs (catchment areas with deep sinkholes and caves) and the high level springs were similar to diffuse springs, they could not distinguish, in terms of chemical variability, between them.

Crowther (1989) used the C_v of Ca^{2+} as a measure of calcium variability at sites where 6 or more water samples were taken in his study of autogenic karst waters in Peninsular Malaysia. C_v's ranged from 0.67% to 34.9% (average of 7.74%), with diffuse seepages having the lowest C_v's. Discharge variability (C_vQ correlated positively with C_vCa^{2+} ($r = 0.65$, $n=112$), and as C_vQ diminished with increasing thickness of overlying limestone, C_vCa^{2+} also decreased.

Hence it can be seen that distinctions between conduit flow springs and diffuse flow springs have been made on the basis of the C_v of total hardness (or calcium hardness or Ca^{2+} concentration in some cases), although setting a precise C_v value to distinguish between conduit and diffuse flow systems appears not to be reliable as they certainly will fluctuate from location to location. One should also bear in mind the following quote from White (1988, p. 208), "The characterisation of the type of flow systems by hardness variations seems to work well for small drainage basins in temperate climates. Large basins (>100 km^2) showed smaller variations even when the spring is known to be fed by conduits, because of longer travel times, the contribution from the diffuse flow part of the system, and the averaging of water chemistries from different parts of the basin."

It must be stressed that the co-efficient of variation of either total or calcium hardness is not the definitive means of classifying spring types, but an indicator that can be used in conjunction with other measurements and observations, e.g. C_v of karst spring water temperatures, known characteristics of caves, degree of calcite saturation, etc. to help delineate spring types (White, 1969; Shuster and White, 1971; Drake and Harmon, 1973; Drake and Wigley, 1975).

In conclusion, karst springs that are fed by allogenic waters which pass into and travel through the limestone in a conduit generally have high C_v parameter values. For a karst spring that is fed physically by a conduit but receives water that is predominantly either diffuse allogenic and/or autogenic recharge C_v parameter values are generally low.

It should be noted here that for the majority of studies that involve the use of data obtained from water samples collected on a regular (e.g. weekly) or a random basis, the water samples collected are generally biased towards baseflow, and hence low variability conditions.

CONDUIT OR DIFFUSE FLOW SYSTEMS ? POSSIBLE MEANS OF DISTINGUISHING BETWEEN FLOW SYSTEMS

Co-efficients of variation for six parameters (as well as median values) are given in Table 6.1 for each of the karst spring and cave water sites sampled (where the number of water samples, n, ≥ 6). Also included for comparative reasons are data from four surface streams (two major and two minor surface streams) and data obtained from the Rural Water Commission (RWC) for the Buchan River for the period 1978-1988 (three monthly data for all parameters except for conductivity and water temperature for which monthly readings are available).

The karst spring and cave water sites can on the basis of similar C_v of total hardness (C_vTothd.) (Table 6.1) be divided into three groups of sites (C_v Ca^{2+} same grouping),

i) New Guinea 2, New Guinea 6 and Moons - 47.5% to 58.8%,

ii) M-4, Scrubby Creek 1 and 2, Dukes and B-67- 19.3% to 24.4%, and

iii) Bitch of a Ditch, Scrooges Vault and B-41- 6.3% to 9.3%.

If a C_vTothd. value of around 10% is used to

TABLE 6.1. MEDIAN AND CO-EFFICIENT OF VARIATION VALUES (C_v %) FOR KARST SPRING, CAVE WATER AND SURFACE STREAM SITES WHERE n ≥ 6. Ca^{2+}, Mg^{2+}, Na^{+}, Cl^{-} AS mg/l; WATER TEMPERATURE (W_T) °C; TOTAL HARDNESS (Tothd.) AS mg/l $CaCO_3$. #RWC - DATA FOR BUCHAN RIVER FROM RURAL WATER COMMISSION.

SITE NO.		Ca^{2+}	Mg^{2+}	Na^{+}	Cl^{-}	W_T	Tothd.
KARST SPRING SITES							
8)	median	25.3	4.8	13.5	19.5	14.0	88.9
	C_v (%)	55.9	59.8	25.0	10.9	11.0	56.2
9)	median	27.1	5.4	13.4	19.2	13.5	92.4
	C_v (%)	61.2	54.1	21.2	12.1	6.9	58.8
10)	median	73.5	14.6	21.7	41.0	13.5	237.0
	C_v (%)	50.8	40.7	23.5	32.2	7.0	47.5
11)	median	98.9	14.1	16.9	37.0	15.0	303.7
	C_v (%)	23.3	26.2	15.8	15.0	10.6	23.1
12b	median	97.8	7.8	16.0	33.0	16.0	279.6
	C_v (%)	23.3	30.8	20.6	24.0	7.9	24.4
13)	median	121.2	37.1	28.8	61.2	17.0	458.9
	C_v (%)	6.4	17.3	19.7	20.5	2.5	9.3
14)	median	157.8	30.5	77.0	211.0	16.9	522.2
	C_v (%)	22.1	25.9	23.2	28.0	5.4	22.9
CAVE WATER SITES							
12a)	median	102.7	7.8	16.1	31.1	16.0	285.1
	C_v (%)	24.5	30.7	21.1	22.2	6.8	23.9
15)	median	120.5	22.9	57.8	180.5	16.5	393.1
	C_v (%)	7.4	19.0	20.1	20.1	4.3	8.6
16)	median	177.6	39.9	104.2	300.2	17.0	611.0
	C_v (%)	19.0	20.7	19.3	21.2	7.4	19.3
17)	median	176.4	40.2	103.2	297.8	16.5	597.4
	C_v (%)	7.3	6.5	8.2	7.7	4.6	6.3
SURFACE STREAM SITES							
1)	median	7.4	2.8	6.7	8.0	14.5	29.8
	C_v (%)	129.4	100.9	75.8	123.2	31.3	113.5
#RWC	median	7.0	2.9	6.6	7.3	14.8	31.5
	C_v (%)	120.5	114.5	73.8	141.6	42.1	112.1

TABLE 6.1 (CONT.).

2)	median	20.2	8.7	16.7	32.9	17.0	93.7
	C_v (%)	43.6	34.7	21.0	24.3	38.4	37.9
4)	median	17.7	13.0	28.7	62.9	13.0	98.9
	C_v (%)	116.3	62.9	31.4	40.1	25.9	89.3
5)	median	68.2	36.6	29.6	64.4	15.5	326.5
	C_v (%)	47.3	43.7	30.5	35.3	36.7	45.3

distinguish between conduit and diffuse flow systems, then the first two of the above three groups of sites would be classified as conduit flow systems (C_vTothd. ranges from 19.3% to 58.8%). The sites in group iii) would be classified as diffuse flow systems.

The conduit flow systems consist of sites from three of the four water TYPES proposed in Chapter Four. The applicability of using the co-efficient of variation of total hardness (C_vTothd.) in this study as a means of distinguishing between flow types, and the critical value of C_vTothd. which distinguishes between conduit and diffuse flow systems will now be examined. This will be determined by looking at how each of the three groups of sites defined above by C_vTothd. respond under different hydrological regimes. The use of C_v's for other parameters, e.g. water temperature, as well as the calcite saturation index will also be examined. As noted by White (p.213, 1988), "The calcite saturation index depends almost entirely on residence time. Open conduit systems permit rapid transmission of water, undersaturated waters appear at the springs, and the system is very sensitive to flushing by storm runoff".

White (p.213, 1988) notes that waters with saturation indices (SI_{cal}) greater than −0.30 generally indicate aquifers with residence times greater than the ≈ ten day period required for calcite to reach equilibrium in the laboratory. Waters sampled in this study with computed SI_{cal} values ≥ -0.30 will be taken to infer diffuse flow conditions operative.

It must be stressed here that the observations noted and inferences made are based on varying numbers of water samples collected from each of the different sites sampled. For example, eight water samples only were collected from New Guinea 2 and New Guinea 6 over the period October 1982 to February 1985 and do not include (due to access problems) samples for the high flow event (July 1984) as do most of the other sites, whereas thirty-one water samples were collected from Dukes over the period October 1982 to May 1988. From the data found in this study for the Buchan River and that obtained from the RWC for this site, it can be seen that the respective median and C_v values do not differ appreciably (Table 6.1), and hence water samples collected in this study would appear to be reasonably representative of the range and values expected even though water samples were not collected on a regular basis. Extrapolating this so that it includes all the karst spring and cave water data would appear to be tenuous, but it is felt that even considering the limitations of some of the data, reasonable conclusions can be made.

KARST SPRING AND CAVE WATER SITES WITH A HIGH CO-EFFICIENT OF VARIATION VALUE FOR TOTAL HARDNESS

New Guinea 2 and New Guinea 6

These two sites stand out quite markedly from the rest of the karst spring and cave sites in that they record the highest C_v's for Ca^{2+}, Mg^{2+} and total hardness.

Median values for most parameters for these two karst spring sites are more similar to those noted for some of the surface stream sites (e.g. Spring Creek and the Murrindal River) than the medians observed at the other karst spring sites. As such these median values reinforce the idea of these two karst springs being fed by conduits. For these two sites, recharge water (predominantly allogenic recharge) is generally shunted through the system quickly and, although aggressive, has little opportunity to increase its dissolved load of Ca^{2+} and Mg^{2+} ions and hence reach equilibrium with the surrounding bedrock. This is also emphasised when looking at, and comparing the Ca^{2+}, Mg^{2+}, alkalinity and SI_{cal} values found at the nearby Un-named Seep site (assumed to have a large diffuse flow component of flow, see below) when all three sites were sampled on the same occasions. On all occasions Ca^{2+}, Mg^{2+} and alkalinity values were notably higher at the seep site (≈ 2 to 5 times for Ca^{2+}, ≈ 3 to 8 times for Mg^{2+} and ≈ 2 to 4 times for alkalinity) than at the two karst spring sites. SI_{cal} values were also notably higher at the seep site and on three occasions were supersaturated with respect to calcite ($SI_{cal} > 0.00$) indicating diffuse flow while SI_{cal} values at the two nearby karst spring sites were < -0.30 indicating conduit flow conditions.

Although these two karst spring sites are assumed to be conduit flow systems it is interesting to note that data obtained on two occasions (February 1983 and February 1985) indicate diffuse flow conditions operating (Table 6.2). Data obtained from the Buchan River for the two above occasions are also included in Table 6.2 to see if the same sort of effects governing water chemistry for the Buchan River were also operative for these two karst spring sites.

As noted in Chapter Three water samples collected in February 1983 were collected during one of the worst droughts experienced in southeastern Australia this century, and as such, are assumed to be representative of the low flow end-member for New Guinea 2 and New Guinea 6 i.e. conditions representative of diffuse flow behaviour.

TABLE 6.2. VALUES OBTAINED FROM NEW GUINEA 2 AND NEW GUINEA 6 IN FEBRUARY 1983 AND FEBRUARY 1985 (MEDIAN VALUES ALSO GIVEN). Ca^{2+}, Mg^{2+}· Na^{+} AND Cl^{-} AS mg/l, SI_{cal} AND SI_{dol} DIMENSIONLESS, ALKALINITY AS mg/l $CaCO_3$ AND WATER TEMPERATURE °C. DATA FOR THE BUCHAN RIVER ALSO INCLUDED.

	Ca^{2+}	Mg^{2+}	Na^{+}	Cl^{-}	SI_{cal}	SI_{dol}	Alkal.	W_T
NEW GUINEA 2								
Feb. 1983	70.1	12.6	14.5	24.0	0.38	0.21	225.1	16.8
Feb. 1985	58.0	11.1	20.0	21.3	0.47	0.38	200.4	14.0
median	25.3	4.8	13.5	19.5	-0.76	-2.08	95.8	14.0
NEW GUINEA 6								
Feb. 1983	73.5	13.1	11.8	17.0	0.15	-0.27	226.9	15.0
Feb. 1985	51.5	8.0	15.5	19.7	0.09	-0.46	169.5	14.0
median	27.1	5.4	13.4	19.2	-0.34	-1.45	95.8	13.5
BUCHAN RIVER								
Feb. 1983	70.1	14.7	26.5	60.0	0.90	1.61	207.2	21.5
Feb. 1985	22.1	5.8	13.3	21.8	-0.45	-1.23	78.0	20.0
median	7.4	2.8	6.7	8.0	-1.40	-3.16	33.0	14.5

All three sites sampled in February 1983 record quite similar Ca^{2+}, Mg^{2+} and alkalinity values and are supersaturated with respect to calcite (New Guinea 2 and the Buchan River also supersaturated with respect to dolomite). For the Buchan River site, which, as noted in Chapter Three had ceased to flow, the high ion concentrations and supersaturation noted are assumed to be mainly due to a concentrating effect due to the drought conditions operating rather than the dissolution of carbonate material. This concentrating effect is most evident in the Na^{+} and Cl^{-} values found on this occasion which are ≈ 4 and ≈ 8 times higher than the respective median values.

For New Guinea 2 and 6 the high Ca^{2+}, Mg^{2+} and alkalinity values noted (≈ 2 to 3 times the respective median) are assumed to be due to diffuse flow conditions operating and not a concentrating effect as noted for the Buchan River (and other surface stream sites sampled on this occasion). This is reflected by the fact that Na^{+} and Cl^{-} values found at both sites are similar to the respective median values, although water temperatures at both sites indicated some warming (2.8°C and 1.5°C above the respective median water temperature for New Guinea 2 and New Guinea 6) but nowhere near the 7.0°C noted for the Buchan River.

Similarly, the data obtained in February 1985 for the two karst spring sites represents diffuse flow conditions operating, with Ca^{2+}, Mg^{2+} and alkalinity being ≈ double the respective median values. The approximate 2 to 3 fold increase in Ca^{2+}, Mg^{2+} and alkalinity values for the Buchan River are also reflected in the Na^{+} and Cl^{-} values and as noted for the 1983 data indicates a concentrating effect.

Of particular interest for these two springs are the notably low C_vCl^{-}, C_vW_T and C_vNa^{+} values when compared to the other C_v values noted at these sites. The most likely reason for the low C_v values for Cl^{-} and Na^{+} is that these two ions are in a more "regular supply" situation than Ca^{2+} and Mg^{2+} ions; i.e. they are not influenced to the same extent as Ca^{2+} and Mg^{2+} ions by whether or not diffuse flow dominates the discharge.

C_vW_T for these two sites are notably lower than any of those observed at the surface stream sites, which most probably is a reflection of a lack of "seasonality" at least for water temperatures, i.e. the spring waters do not undergo the wide range of temperature fluctuations, hence variability, experienced by the surface stream waters. "Seasonality" will be discussed in more detail later in this Chapter.

For these two karst spring sites the high Cv associated with total hardness (and Ca^{2+}) used in conjunction with the median calcite saturation index best describes conduit flow conditions. Water sample analysis shows that conduit flow predominates for the majority of the time although under low recharge conditions, the diffuse flow component becomes increasingly more important, as indicated by the saturation index for calcite. C_v of water temperature is a useful parameter for distinguishing between karst spring waters and surface waters that have similarly high C_v values of total hardness (or Ca^{2+}). This interpretation is consistent with observations made, and knowledge of these sites.

Moons

In Chapter Four this site was noted to lie between water TYPES 1 and 2. C_v's for Ca^{2+}, Mg^{2+} and total hardness certainly lie closer to those noted for the two New Guinea karst spring sites (and Back Creek and the Murrindal River) than those for the other karst spring and cave water sites and would tend to indicate a predominantly conduit flow system.

If, as for New Guinea 2 and New Guinea 6 an SI_{cal} value ≥ -0.30 is taken to infer diffuse flow conditions, then for this site diffuse flow conditions were operating 62% of the time this site was sampled, i.e. 18 out of the 29 samples collected at this site recorded SI_{cal} values ≥ -0.30 (median SI_{cal} value = 0.11).

This site responds quickly to high rainfall events, in which water chemistry (as well as the water temperature and the saturation index with respect to calcite) dramatically alters and conduit flow predominates. As such it is a good example of a mixed conduit/diffuse flow system. An example of this quick response time and rapid change from diffuse flow to conduit flow conditions is best exemplified by comparing data obtained at this site with that obtained from two nearby sites (Spring Creek and Dukes), all of which were sampled over a four day period in November-December 1987.

In Figure 6.1 Ca^{2+}, HCO_3^-, SI_{cal} and water temperature values are plotted against time for Spring Creek, Moons and Dukes which were sampled on day 1 (≈ 1800), and day's 3 and 4 (≈ 1200) following 57mm of rainfall in a 12 hour period on day two. Additional water samples were collected from both Moons and Dukes at ≈ 0800, 1200 and 1600 on day 3 and ≈ 0800 on day 4. Also shown in Figure 6.1 is the discharge hydrograph recorded by a Stevens Water Level Recorder (Model 71A) set up at Dukes outlet (1/2 90° v-notch weir; BSI, 1981).

DAY 1 For Spring Creek and Moons, Ca^{2+}, HCO_3^-, water temperature and SI_{cal} values were either the same as the respective median value or higher.

At Dukes, Ca^{2+}, HCO_3^- and SI_{cal} values were slightly lower than the respective median value with water temperature being the same as the median value.

DAY 3 Following the 57mm of rainfall on day 2, the water chemistry at Spring Creek and Moons was dramatically different to concentrations noted for these two sites on day 1. Both sites were cooler, Moons only marginally, and undersaturated with respect to calcite.

At Dukes constituent levels were approximately the same (also water temperature) as that recorded for day 1 although discharge had increased roughly 6 fold (Figure

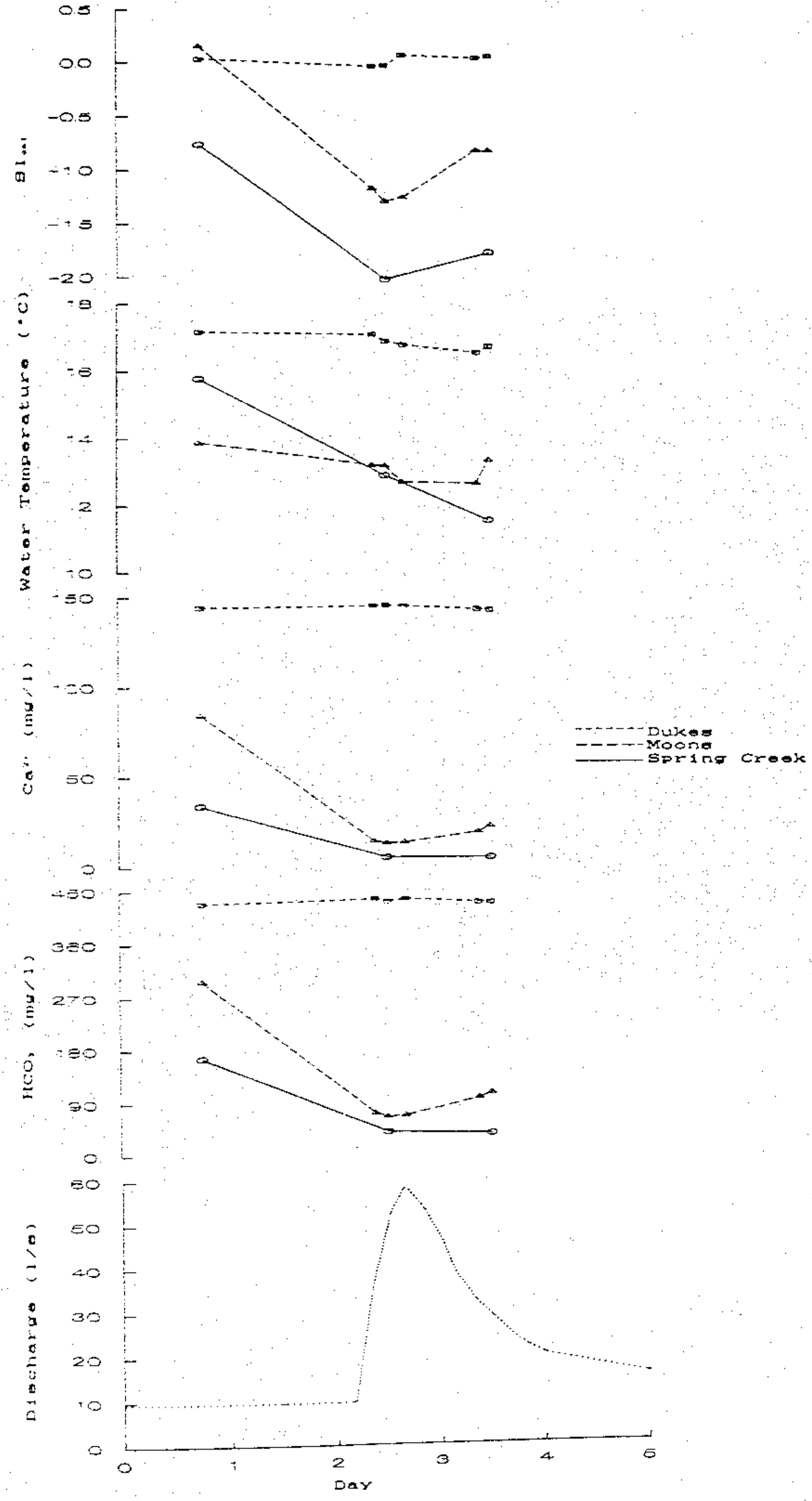


Figure 6.1. Changes in Ca^{2+}, HCO_3^-, water temperature and SI_{cal} values for Spring Creek, Moons and Dukes for the period 30th November to 3rd December 1987. Discharge hydrograph for Dukes also shown. Note 0 on x-axis = 0000 hours on 30th November.

6.1); water just out of equilibrium with respect to calcite (SI_{cal} = −0.01).

Discharge for all three sites increased with Spring Creek and Moons showing the most dramatic increases; at these two sites large volumes of highly turbid water were observed. The water at Dukes remained quite clear. Unfortunately no discharge data is available for Spring Creek and Moons to indicate when peak discharge occurred, and observations are strictly limited to noting the "water level" when each site was sampled. For Dukes however, peak discharge for this site was noted to occur at 1500 on day 3 with a value of 58.3 l/s compared with a mean value of 9.6 l/s on day 1 (Figure 6.1). For Moons the highest "water level" was noted to occur when the 1600 hour water sample was collected on day 3. It must be stressed here that the "water level" noted at Moons is solely based on observations made when water samples were collected on the five occasions between ≈ 0800 (day 3) and ≈ 1200 (day 4).

DAY 4. Constituent levels at Spring Creek were virtually unchanged from those noted on day 3 although water temperature was cooler. At Moons, Ca^{2+} and HCO_3^- were marginally higher than the respective day 3 values. For Dukes virtually no change in chemical values; this lack of "chemical response" noted is discussed in more detail later in this Chapter.

It would appear then, that at least for Moons and Dukes, that although the response time to high rainfall events may be similar, the chemical composition of the discharging water certainly differs and this is very dependent upon how recharge is transmitted through the respective systems.

The rapid response to the high rainfall event noted at Moons is almost a copy of the response noted at Spring Creek. This indicates that recharge to this particular karst spring can on occasions be rapidly transmitted through the system. It is hypothesised that a particular recharge threshold exists which, once exceeded, activates flow paths that are normally inactive. An example of this behaviour could be Spring Creek itself.

For the majority of the time Spring Creek downstream of where it is sampled is a dry stream channel. Only after high or prolonged rainfall events does it become active and depending upon the type of event floodwaters 1-2m in depth have been noticed. The rapid change from diffuse flow to conduit flow conditions noted at Moons site could be partially explained by the channelling of floodwater from Spring Creek via activated flow paths into the Moons Cave system, although it is not possible to distinguish between this floodwater and storm runoff derived from the nearby Snowy River Volcanics with the available data. White and Davey (1977) established a link between a septic tank outflow (located along the bank of Spring Creek) and the stream passage in Moons Cave and this could be one of the flow paths activated. Fluorescent dye tracing experiments under "normal flow conditions" in Spring Creek, i.e. where the water sinks (site 4), have failed to prove (or disprove) any connection between these two systems.

If the C_v of total hardness was alone used to classify this site it would be classified as having predominantly conduit flow. However SI_{cal} values obtained tend to dispute this and as such this site is classified as a mixed conduit/diffuse flow system.

As noted for New Guinea 2 and New Guinea 6 the C_v of water temperature is a useful parameter for distinguishing between karst springs and surface waters that have similar high C_vTothd. values.

KARST SPRING AND CAVE WATER SITES WITH A MEDIUM CO-EFFICIENT OF VARIATION VALUE FOR TOTAL HARDNESS

For this group of sites although C_vTothd. indicates conduit flow, all sites record median SI_{cal} values ≥ 0.00 which as noted previously is assumed to infer diffuse flow conditions. The most interesting observation about this group of sites is that over the period they were sampled (October 1982 - May 1988) SI_{cal} values < -0.30

were only recorded for water samples collected in both July and September 1984 for M-4 and Scrubby Creek, July 1984 for B-67 and September 1984 for Dukes.

As noted in Chapter Three water samples collected in July 1984 are assumed to be representative of the high flow end-member of possible flow regimes. Rainfall for the first six months of 1984 (January 1st to June 30th) was 354mm, slightly below the long term average of 393mm. Rainfall for July 1984 up until the day before the sites were sampled was 107mm (compared with a monthly mean of 66mm) with another 110mm of rain falling over the two day period the sites were sampled. Unfortunately no chemical or physical data were collected before the high rainfall event to determine what, if any effect the already above average rainfall for July had had on parameter values at the sites sampled.

The lowest Ca^{2+}, Mg^{2+}, Na^{+}, Cl^{-}, alkalinity, total hardness and water temperature (all sites except M-4) values detected at the above sites are all associated with water samples collected in July 1984. The second lowest values for the above parameters are associated with the September 1984 water samples. It would appear that the water samples collected in September were still being influenced to some extent by recharge waters from the flood event at the end of July although to what extent is hard to determine. Rainfall for August was slightly below the long term mean, 54mm compared with 60mm, and up until the water samples were collected in September, rainfall was below the monthly mean.

In Figure 6.2, expressed as a percentage of the respective median value for Ca^{2+} and alkalinity, data are plotted against day of the year for water samples collected in May (day 137) before the high flow event in July (day 211) and for water samples collected in September (day 260) and November (day 320). SI_{cal} values are also plotted against day of the year. The data presented is important because it gives a rough indication of the "recovery time" of each of these sites over this period, i.e. time required for parameter values to return back to approximate background levels (median values). This "recovery time" is assumed to be a reflection of each sites ability to return to "normal" following a high flow event, which in turn is an indication of how long it can take storm water from a particular storm event to be completely transmitted through the system.

All sites, except Dukes, had Ca^{2+} and alkalinity concentrations roughly equivalent to the respective medians at least by the time water samples were collected in November 1984, if not earlier (Figure 6.2). The lower Ca^{2+} and alkalinity values noted at Dukes are not easily explained but they could possibly be related to some high

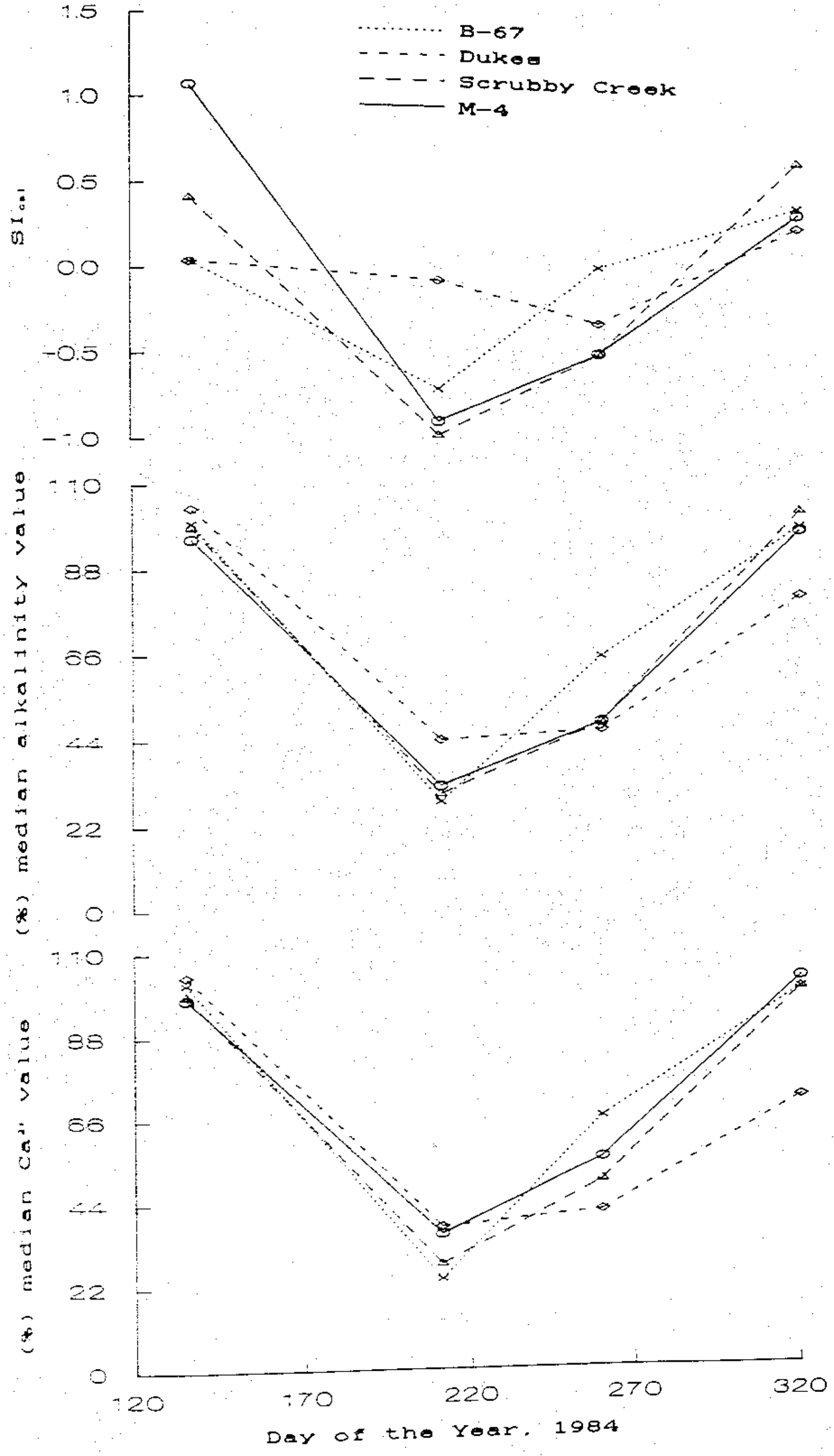


Figure 6.2. Changes in Ca^{2+} and HCO_3^- concentrations represented as a proportion (%) of the respective median value for the period May to November 1984 for M-4, Scrubby Creek, Dukes and B-67. SI_{cal} values recorded over the same period also shown.

flow event water still making its way through the system. As noted previously, water from B-67 has been linked to water exiting at Dukes with a lag time of ≈ 24 days under "normal" flow conditions (i.e. discharge at Dukes is ≈ 4.0 l/s). Therefore although B-67 chemical values were back to around median levels in November, this "background water" had not yet reached Dukes.

As noted above, and in Chapter Four, the effect of the July 1984 high flow event on all sites sampled was quite dramatic. It is interesting to note that if the July and September 1984 data are omitted from the data sets gathered from each site in this group, quite significantly different C_vTothd. values are obtained. C_vTothd. values of 11.6%, 10.3%, 12.6% and 3.2% are obtained for M-4, Scrubby Creek, Dukes and B-67 respectively compared with C_vTothd. values of 23.1%, 24.4%, 22.9% and 19.3%. C_vW_T also differs noticeably for all sites except M-4 if the July and September 1984 data is omitted. For Scrubby Creek, Dukes and B-67 the values are ≈ halved (3.6%, 3.1% and 4.0% compared with 7.9%, 5.4% and 7.4% respectively) whereas for M-4 the difference is much less (9.6% compared with 10.6%). The small difference noted at M-4 is attributed to the fact that this site drains a relatively smaller and shallower groundwater aquifer than the other sites and appears to be more "seasonally" affected than the other karst spring and cave water sites. This is reinforced by the fact that

M-4 is the only karst spring site that flow was noticed to have ceased on four different occasions when flow was detected at all other karst spring and cave water sites.

It can be seen then that although a particular C_vTothd. or C_vW_T value can be obtained for a particular site it can only be used as an approximate measure unless water samples collected are proportionally representative of all flow conditions.

For the sites in this group then, a C_vTothd. of ≈ 10% to distinguish between predominantly diffuse flow and predominantly conduit flow systems is unrealistic. These sites display diffuse flow behaviour practically all the time and only rarely is conduit flow behaviour displayed. It would appear then that a C_vTothd. value of ≈ 24% is more appropriate, at least for the sites in this group to distinguish between predominantly diffuse flow systems and mixed conduit/diffuse flow systems.

KARST SPRING AND CAVE WATER SITES WITH A LOW CO-EFFICIENT OF VARIATION VALUE FOR TOTAL HARDNESS

In any discussion about the sites in this group it is important to remember that Scrooges Vault and B-41 have only been sampled since May 1985 and as such no data is available that is representative of high flow conditions.

Bitch of a Ditch is the **only site** sampled that records SI_{cal} values > 0.00 on all sampling occasions, even for water samples collected in July and September 1984, and as such is assumed to be the only true diffuse flow system examined in this study, no matter what recharge conditions apply in its catchment.

What effect a high flow event would have had on water chemistry at Scrooges Vault and B-41 is difficult to determine. Certainly at B-67, which is located nearby, a dramatic decrease in chemical concentrations (when compared to median chemical values) were noted. The fact that median parameter values at B-67 and B-41 are almost identical tends to suggest they are the same body of water (see Chapter Five) and that water at B-41 would show the same response noted at B-67. For Scrooges Vault with the data available it is almost impossible to determine.

For Bitch of a Ditch, C_vTothd. and C_vW_T values in conjunction with SI_{cal} values adequately describe the diffuse flow nature of this system. If the July and September 1984 data are omitted from the data set for this site C_vTothd. is ≈ halved (4.3% instead of 9.3%) whereas C_vW_T remains virtually the same (2.3% compared with 2.5%).

The C_v's obtained in this study for the karst spring, cave water and surface stream sites, particularly those for Ca^{2+} and total hardness, have a much greater range than those published in the literature (see discussion at the start of this Chapter). Two explanations are possible.

The higher C_v values noted in this study could possibly be related to the fact that the study area is a comparatively small impounded karst with all surface waters having their origin on Snowy River Volcanics and cannot be directly compared to an extensive karst area.

The higher C_v values obtained in this study could also simply be a reflection of the greater variability inherent in many Australian systems (McMahon, 1982; Finlayson et al, 1986; Finlayson and McMahon, 1988; Kuhnel et al, 1990), in which C_v values for rainfall and discharge of 25% and 65% respectively are not unusual.

A value of around 10% for C_vTothd. (or C_vCa^{2+}) to distinguish between diffuse flow and conduit flow systems as suggested by Shuster and White (1972) is not applicable in this study. A C_vTothd. value used in conjunction with C_vW_T and a median SI_{cal} value are suggested as the minimum three variables needed before a reasonable assessment of each sites flow characteristics can be made.

Examining the physical and chemical evidence for the karst spring and cave water sites it would appear then that no site displays conduit flow behaviour over the whole range of hydrological conditions experienced during this study, particular those operating under drought conditions. Only one site (Bitch of a Ditch) displays diffuse flow behaviour over the range of hydrological regimes.

Ranking the karst spring and cave water sites (by using C_vTothd. (%), C_vW_T (%) and median SI_{cal} values) into sites ranging from diffuse flow domination through to conduit flow (Spring Creek used as an example) domination is as follows:

DIFFUSE FLOW	C_vTothd.	C_vW_T	SI_{cal} (median)
BITCH OF A DITCH	9.3	2.5	0.62
SCROOGES VAULT	8.6	4.3	0.19
PREDOMINANTLY DIFFUSE FLOW			
B-67 (B-41)	19.3 (6.3)	7.4 (4.6)	0.27 (0.27)
DUKES	22.9	5.4	0.23
SCRUBBY CREEK	24.4	7.9	0.54
M-4	23.1	10.6	0.52
MIXED FLOW			
MOONS	47.5	7.0	0.11
PREDOMINANTLY CONDUIT FLOW			
NEW GUINEA 6	58.8	6.9	-0.34
NEW GUINEA 2	56.2	11.0	-0.76

MINOR SURFACE STREAM			
SPRING CREEK	116.3	25.9	-1.05

As noted in Chapter Five the spatial variation in median water temperature for the karst spring and cave water sites was assumed to be related to catchment aspect and vegetation cover. Correlation of median water temperature and C_vTothd. for the karst spring and cave water sites indicates a negative relationship (r = 0.904, significant at 99.97% level). This relationship,

$\log W_T = 1.244 - 0.002 C_v\mathrm{Tothd.}$, indicates that the residence time of water is also an important factor in influencing water temperature for the karst spring and cave water sites: diffuse flow - higher median water temperature; conduit flow - lower median water temperature.

SURFACE STREAM SITES

For the Buchan River and Spring Creek, C_v's for all parameters are higher than any of the corresponding C_v values noted for any of the karst spring and cave water sites, particular so for C_vCa^{2+}, C_vW_T and C_vTothd.. For the Murrindal River and Back Creek, C_vCa^{2+}, C_vMg^{2+} and C_vTothd. values are noted to lie between those values observed for three karst spring sites (New Guinea 2, New Guinea 6 and Moons) and those values noted for the remaining karst spring and cave water sites. This is assumed to indicate the importance of groundwater contribution to sustaining flow at these two surface stream sites.

All four surface stream sites have quite significantly higher C_vW_T values when compared to the range of values found for this parameter at the karst spring and cave water sites, and it would appear that perhaps this parameter is the most important in distinguishing between surface and sub-surface flow. The higher C_vW_T value noted at the surface stream sites is primarily attributed to seasonality i.e. fluctuations in air temperature. How important the role of seasonality is in explaining any of the variability noted at the karst spring and cave water sites is examined later in this Chapter.

CHEMICAL RESPONSE OF KARST SPRING WATERS TO PARTICULAR HYDROLOGICAL REGIMES

In this section the chemical response noted at the karst spring sites under low flow and high flow regimes is examined and compared with "median flow" values to, i) see if the same response patterns operate for the different karst spring categories defined by C_vTothd., and ii) to postulate possible flow mechanisms for the different karst spring categories. Rather than examine each site individually one site only is selected from each category and is assumed to be, in general, representative of karst spring in that particular category.

Data gathered from Moons and Dukes over a four day period (November 30th - December 3rd 1987) is also examined briefly at the end of this section.

In Figure 6.3 ionic proportions (%) of the major cations and anions (as meq/l) for the two end-members of possible flow regimes (low flow and high flow) as well as "median flow" are shown for the different karst spring categories. Low flow results for all sites are from water samples collected in February 1983. High flow results are from water samples collected in July 1984 for Moons and Scrubby Creek, and in September 1984 for New Guinea 6 and Bitch of a Ditch.

LOW FLOW CONDITIONS

Under low flow conditions Ca^{2+} and HCO_3^- are the dominant cation and anion respectively for all karst spring categories. In Chapter Four it was noted that similar trends could be found for the major and minor surface stream sites.

For the predominantly conduit flow springs (e.g. New Guinea 6) ionic proportions of Ca^{2+}, Na^+, K^+, Cl^- and

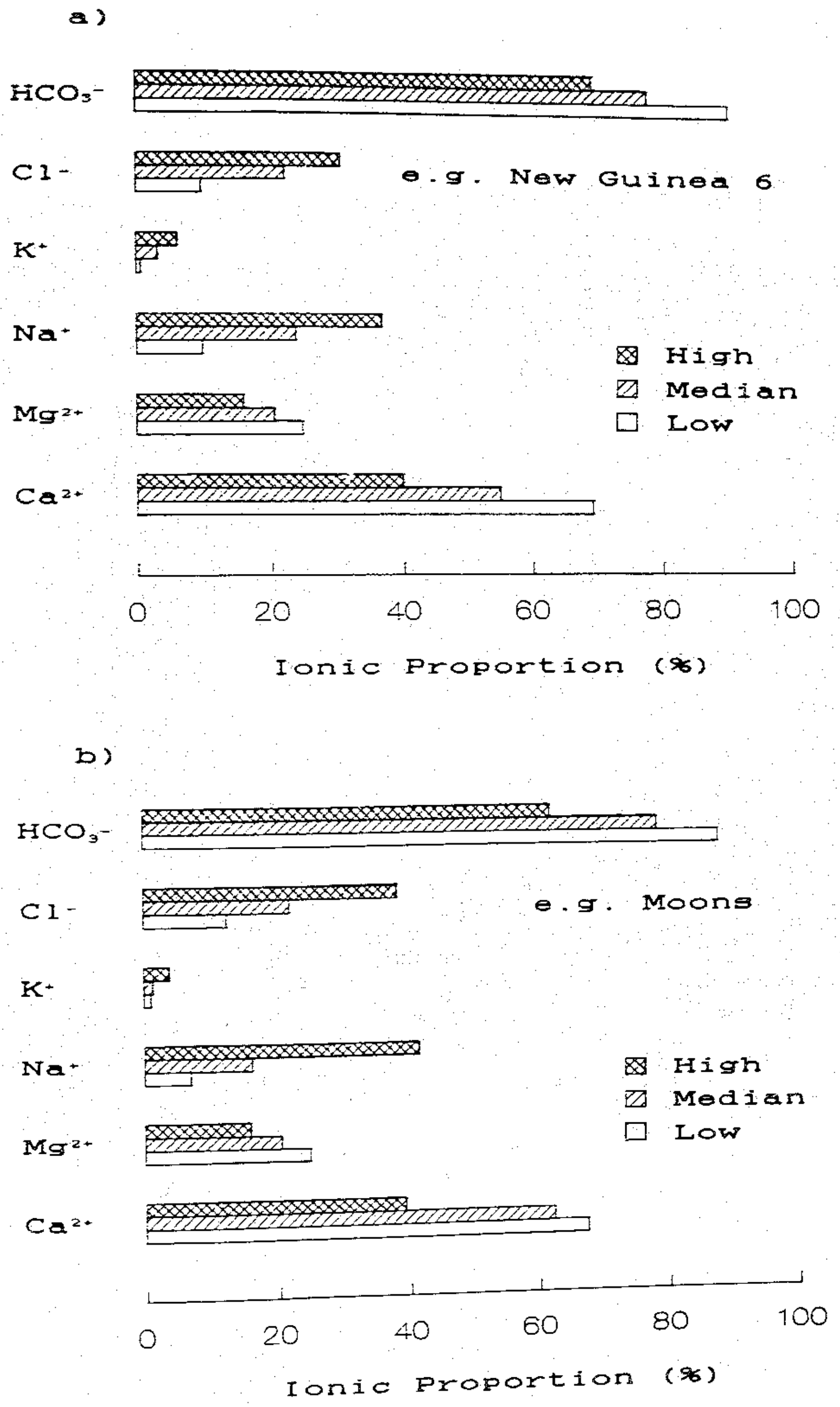


Figure 6.3. Ionic proportions (%) of major cations and anions for low, median and high flow regimes. a) an example of a predominantly conduit flow system, and b) an example of a mixed conduit/diffuse flow system.

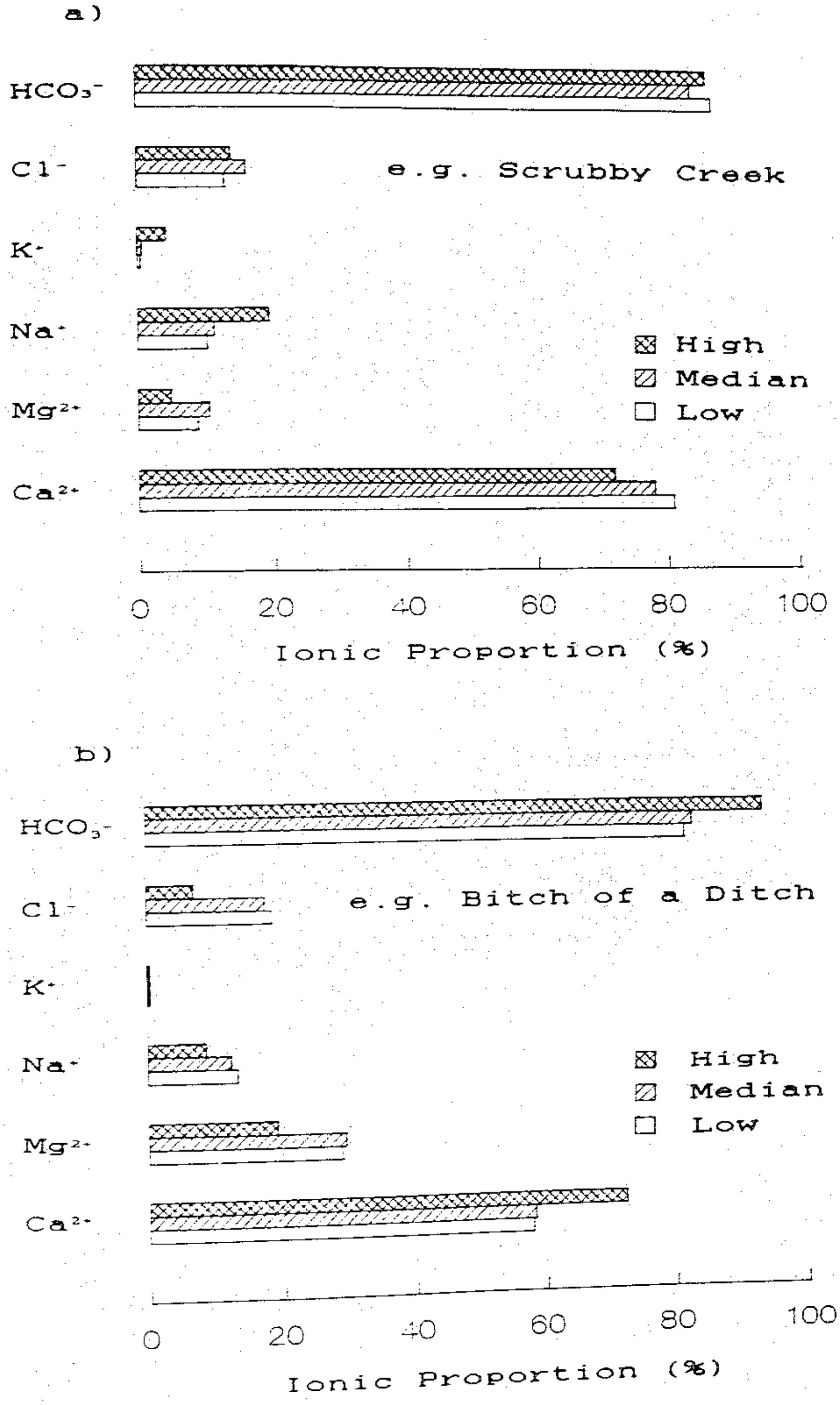


Figure 6.4. Ionic proportions (%) of major cations and anions for low, median and high flow regimes. a) an example of a predominantly diffuse flow system, and b) an example of diffuse flow system.

HCO_3^- under low flow conditions differ quite markedly from median ionic proportions. The notable increase in Ca^{2+} and HCO_3^- proportions are assumed to be due to increased dissolution of carbonate material due to the diffuse flow component of flow dominating. Although most recharge for this category of karst springs is derived from the Snowy River Volcanics (allogenic recharge) which are assumed to have little water storage capacity in comparison to the limestones, flow persisted in February 1983 when a number of surface stream sites and a karst spring site (M-4) had ceased to flow. It appears then, that for this category sufficient storage capacity exists to sustain baseflow even at times of maximum water stress. It is hypothesised that this water storage exists almost entirely in the limestone component of each sites catchment and occurs in what Williams (1983) terms the subcutaneous zone. Williams (1983) found that the subcutaneous zone (upper weathered layer of rock beneath the soil profile, but above the phreatic (permanently saturated) zone) has a high degree of secondary permeability and is quite important in karst hydrology and that water storage in this zone should at least be considered a possible component of a karst spring sites ability to sustain baseflow.

For Moons (mixed conduit/diffuse flow), Ca^{2+}, Mg^{2+} and HCO_3^- proportions are marginally higher than the median proportions indicating an increase in limestone dissolution due to diffuse flow dominating. As for the predominantly conduit flow karst springs, that this site was still flowing in February 1983 is attributed to sufficient water storage capacity existing in the subcutaneous zone.

For the predominantly diffuse flow sites (e.g. Scrubby Creek) and Bitch of a Ditch (diffuse flow) ionic proportions vary only slightly between the result obtained for the low flow end-member and the result obtained using median values. This again reinforces the idea that for these sites, diffuse flow is the rule rather than the exception.

HIGH FLOW CONDITIONS

Under high flow conditions ionic proportions of Na^+ and Cl^- become increasingly more important (at the expense of Ca^{2+} and HCO_3^- ionic proportions) for the predominantly conduit flow and mixed conduit/diffuse flow karst springs. This is assumed to be due to the quick response of these sites to high flow event water derived primarily from Snowy River Volcanics (allogenic recharge). For New Guinea 6 it is also quite noticeable that cation and anion proportions found under high flow conditions, except perhaps for K^+, are closer to median proportions than those found under low flow conditions indicating more "normal" conditions.

For the predominantly diffuse flow sites although the Na^+ proportion ≈ doubles, the Ca^{2+} proportion is only slightly lower. For the anions when compared to the median proportions, only minor changes are noted.

For the diffuse flow site, it is the only site at which the Ca^{2+} and Na^+ proportions significantly increased and decreased respectively when compared to the respective median proportions. Mg^{2+} proportion also notably lower than the median proportion. The decrease in Cl^- proportion and increase in HCO_3^- proportion (when compared to median and low flow proportions) is attributed to the mixing of storm water with old pre-storm water. The dilution noted is due to the "shunting" or "flushing" of old pre-storm water (median parameter values) from the vadose zone (e.g. subcutaneous zone) and its subsequent mixing with the more dilute rapidly arriving storm water. The fact that Bitch of a Ditch had in general, lower chemical values in September 1984 rather than July 1984 is obviously a reflection of how much slower storm water is transmitted through this system when compared to transmission times for the other karst spring categories.

NOVEMBER - DECEMBER 1987

As noted previously in Chapter Four and also in this Chapter, Moons and Dukes were each sampled on six occasions over a four day monitoring period in November-December 1987 with 57mm of rainfall falling on day two. The results obtained over the four day period reinforce the idea of Moons showing a very rapid response to rainfall events of a particular magnitude and intensity (Figure 6.5).

Water at Moons changed from a Ca^{2+} - HCO_3^- dominated water type on day 1 to a Na^+ - $HCO_3^- \approx Cl^-$ type water on day 3 to a $Ca^{2+} \approx Na^+$ - HCO_3^- type water on day 4. The change in cation and anion proportions on day's 3 and 4 when compared to day 1 are attributed to the rapid arrival and mixing of storm water with pre-storm water. The "shunting" or "flushing" of old pre-storm water through the system by storm water appears to be completely overwhelmed by the rapid arrival of allogenic storm water.

In marked contrast, chemical constituent values (hence ionic proportions) remained virtually constant at Dukes over the sampling period (see Figure 6.1) although discharge increased ≈ 6 fold (see previous discussion on Moons). The fact that chemical constituent values remained constant indicates no mixing of old pre-storm water with storm water. This is attributed to the "flushing" or "shunting" of old pre-storm water from the epikarstic zone by storm water with a distinct pulse. As noted by Ford and Williams (1989, p.160-161) "Diffuse

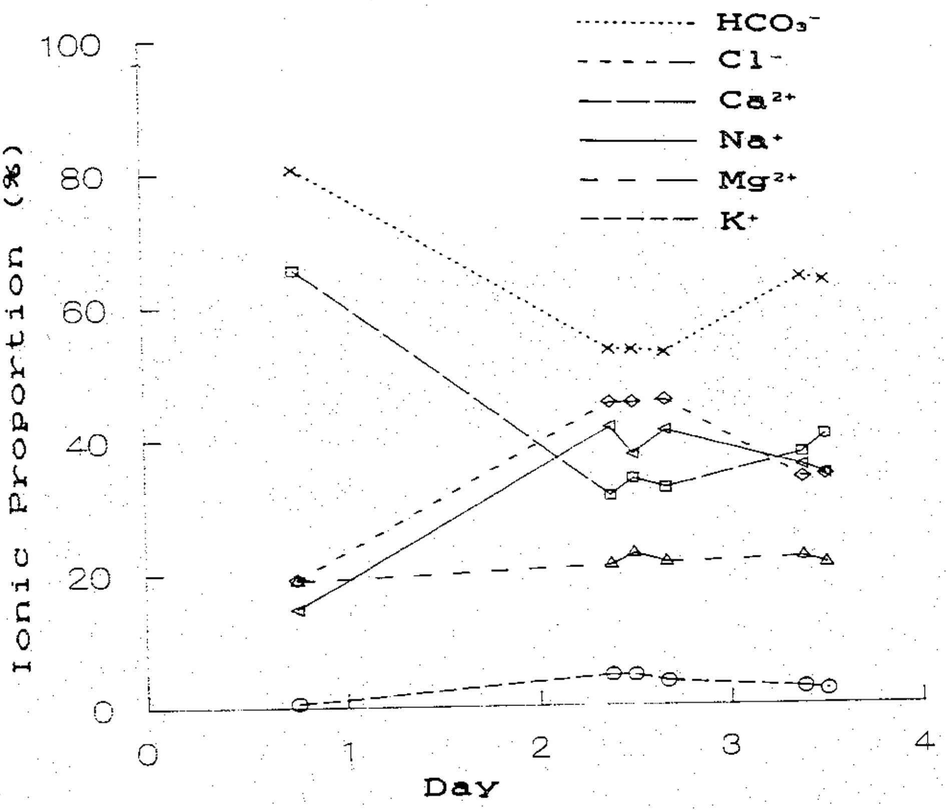


Figure 6.5. Changes in ionic proportions (%) of major cations and anions noted at Moons over the period 30th November to 3rd December 1987. (Note 0 on the x-axis = 0000 hours on the 30th November.

autogenic recharge can also generate pulses in percolation throughput, although some of the water displaced may be many months old due to storage in the epikarstic aquifer". Unfortunately only a limited number of water samples were collected during the recession limb of the hydrograph and as such one is unable to determine when storm derived recharge appeared at the spring. Although the storm hydrograph from Dukes is typical of that depicted in the literature for a conduit flow spring the chemical evidence supports the predominantly diffuse recharge nature of this site.

It can be seen then that for Dukes a more careful interpretation is needed to distinguish between discharge peaks related solely to high intensity rainfall events and those reflecting a combination of "new" storm derived recharge and "old" water already in transit through the system. As well as recording stage height other parameters such as water temperature, electrical conductivity and turbidity need to be continuously monitored, particular over the peak and recession parts of the hydrograph before being able to distinguish between the different flow components. Driess (1989) in her study of three karst springs in Missouri found that by using a cation balance of "old" prestorm karst water and "new" storm water one could determine the component of, assuming straight forward mixing, of "new" water as a proportion of the total discharge. She also noted (p.124), "The maximum chemical perturbation occurs during the recession of the spring discharge hydrograph and represents the arrival of relatively dilute water at the spring outlets".

SEASONALITY

If mean monthly air temperature data (obtained from the Bureau of Meteorology for Orbost or Nowa Nowa) is plotted against month of the year (Figure 6.6) a seasonal trend is observed with warmer and cooler mean air temperatures occurring during the summer and winter months respectively. Similarly using monthly water temperature data for the Buchan River obtained from the RWC (n=152), a seasonal trend is observed (Figure 6.6) in which, as expected, lower water temperatures generally coincide with the winter months, with higher water temperatures occurring during the summer months.

Both the mean monthly air temperature and the water temperature plots approximate cosine curves. Taking into account the lag effect of actual air temperature behind the solar seasons it is possible to compute a regression equation that accounts for the greatest amount of variation. For both mean monthly air temperature and water temperature the line of best fit approximates a cosine curve with a lag time of 25 days i.e. there is a seasonal lag of 25 days. For mean monthly air temperature (A_T) the line of best fit is,

$A_T = 14.374 + 4.833(\cos(\text{day}-25))$, $(n = 39,\ r = 0.922)$.

For Buchan River water temperature (W_T) the line of best fit is,

$W_T = 13.938 + 7.718(\cos(\text{day}-25))$, $(n = 152\ ;\ r = 0.958)$.

Both significant at the 99.9% level.

Discharge for the Buchan River is also seasonal with the highest mean monthly discharge (megalitres, ML) occurring mid-spring (October - 22,900 ML) and the lowest mean monthly discharge in early autumn (March - 4,900 ML). Mean discharge for the three winter and the three

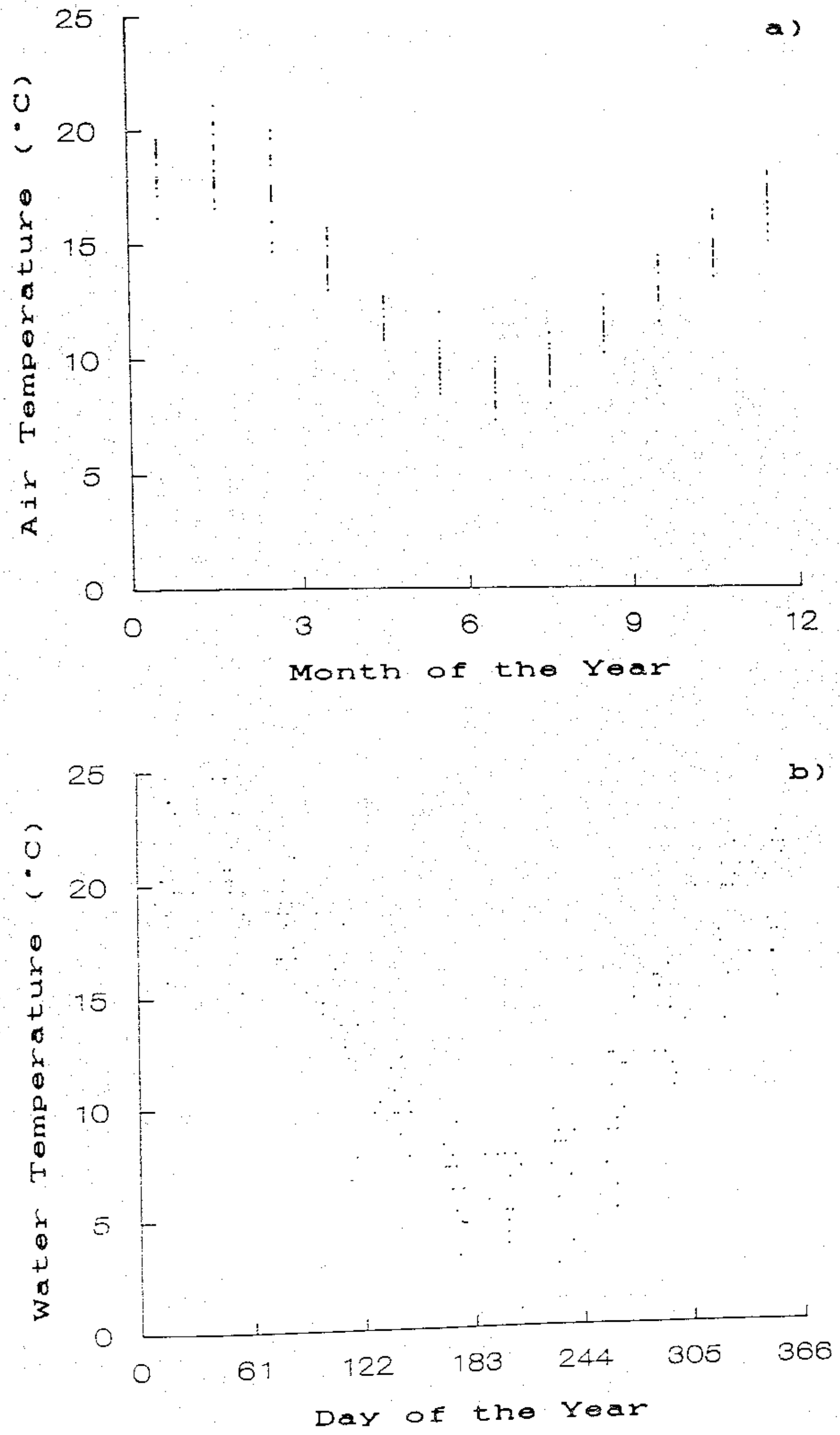


Figure 6.6. Scatterplots of a) mean monthly air temperature (°C) against month of the year (Orbost data), and b) Buchan River water temperature (°C) against day of the year. Data sources: Bureau of Meteorology and Rural Water Commission.

spring months is 53,800 ML and 61,100 ML respectively, indicating a slight springtime domination over winter discharge (summer and autumn discharges are 25,330 ML and 23,740 ML respectively). Using the classification of river regimes proposed by Haines et al (1988), the Buchan River would be classified as being a, Group 14: Early Spring type river regime system. As noted in Chapter 2, mean monthly rainfall is relatively uniform throughout the year with the driest and wettest months being February (58mm) and October (79mm).

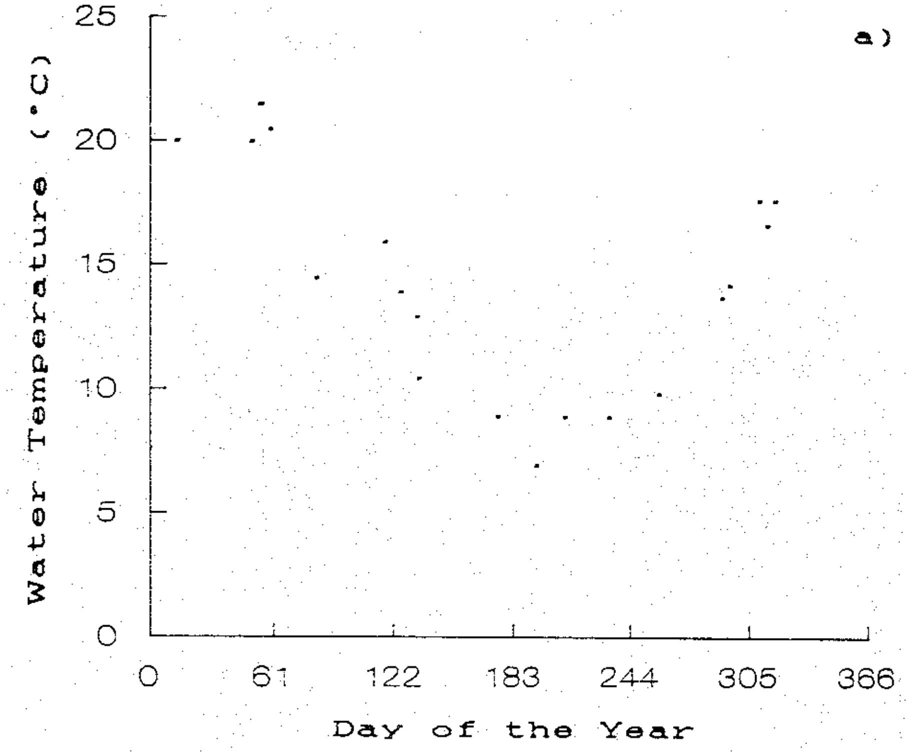
Therefore for the study area seasonality does exist, at least for air and water temperature and discharge whereas rainfall is "non-seasonal", i.e. there is no distinct wetter or drier period. Unfortunately no monthly soil carbon dioxide measurements are available to assess "seasonality" in the soil profile. If any soil carbon dioxide measurements were available it is hypothesised that higher values would be expected to occur in the peak growing periods of late-winter to early-summer and also perhaps in mid to late-autumn, periods in which potential evapotranspiration is relatively low (minimum water stress) (see Table 2.4) and biological activity at a maximum. As noted in Chapter One, many authors (see references in Chapter One) consider soil CO_2 levels, produced in the near-surface zone, the major control on CO_2 levels in karst waters. According to White (p. 213, 1988), "Near-surface processes are strongly influenced by climatic variables (or one could say that CO_2 production **is** a climatic variable)". He also states that," The seasonal oscillation in CO_2 partial pressure observed in soils and cave atmospheres also appears in the chemistry of karst waters", if this seasonality exists then the log(PCO_2) values computed for karst spring and cave water sites in this study would be expected to show this.

To see if the above "seasonal signal" is evident in the data collected from the karst spring sites in this study, water temperature and log(PCO_2) values were correlated against cos(day) and sin(day) of the year on which data was collected. A cosine curve is assumed to approximate seasonality for water temperature and a sine curve is assumed to approximate seasonality for log(PCO_2). To determine seasonal lags, if any, a multivariate general linear model was used to model an equation accounting for the most variation with lag times ranging from 5 to 85 days (in 5 day steps) for both cosine and sine curves.

Buchan River data was also used to see if the data collected in this study compared favourably with that obtained from the RWC (water temperature data only) indicating no specific sample bias. Moons, M-4, Bitch of a Ditch and Dukes were selected as they best represent the karst spring sites sampled and the length of period over which the sites were sampled. The four karst spring sites also represent three out of the four water types proposed (TYPES 2, 3 and 4) and three out of the four possible flow systems (mixed conduit/diffuse flow, predominantly diffuse flow and diffuse flow). The data for sites with TYPE 1 water (New Guinea 2 and New Guinea 6) is limited (no high flow data) and has not been considered here although out of the karst spring and caves water sites sampled, they are mostly likely to be the most "seasonal", i.e. their predominantly conduit flow nature more closely resembles that of the minor surface streams.

Water temperature and log(PCO_2) plots for the Buchan River (Figure 6.7) both show a strong seasonal signal. For water temperature a cosine curve with a lag of 25 days explains 92.5% of the variation noted (significant at the 99.9% level). A sine curve with a lag of 25 days accounts for 53.3% of the variation noted in log(PCO_2) values (significant at the 99.9% level).

Comparing plots of water temperature and log(PCO_2) values against day of the year for the four karst spring sites (Figures 6.8 to 6.11) with those obtained for the Buchan River, any seasonal signal would appear to be much less subdued if present at all. Moons and M-4 record C_v's of water temperature of 7.0% and 10.6% respectively and if a "seasonal signal" does exist in karst spring water



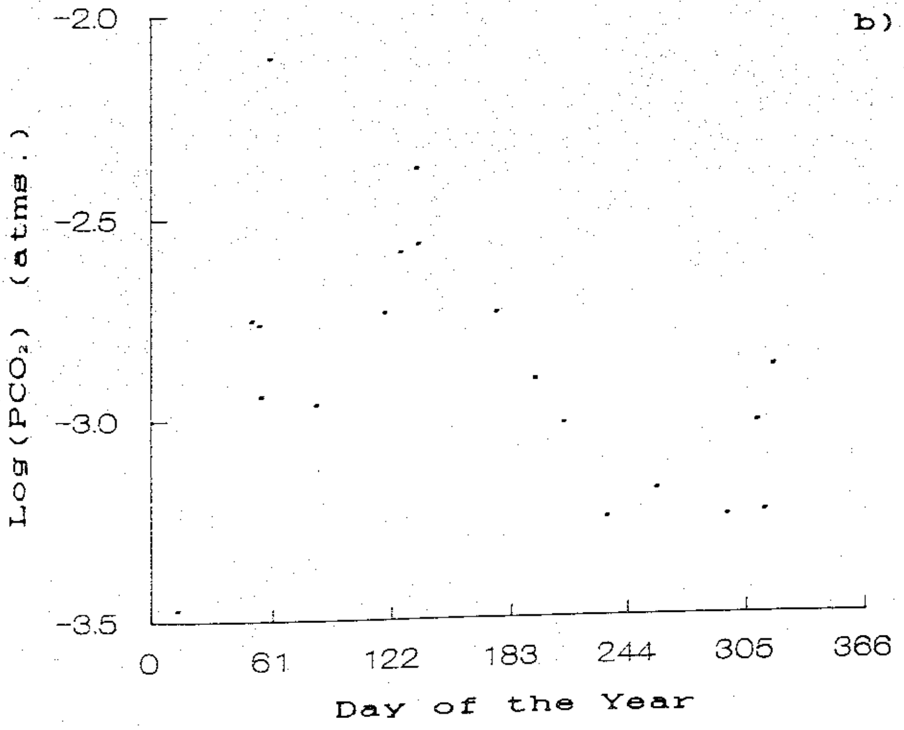


Figure 6.7. Scatterplots of a) water temperature values (°C), and b) log(PCO_2) values (atms.), against day of the year on which data was collected for the Buchan River.

temperatures it should be evident at least at these two sites.

Moons spring is the most "seasonal" of the karst spring sites (significant at the 99.9% level) with 42.3% of the variation in water temperature being accounted for by a cosine curve with a lag of 70 days. The longer lag time at this site when compared to the seasonal lag noted for the Buchan River, is attributed predominantly to delay times in groundwater storage at this site (i.e. the diffuse flow component) rather than the conduit flow component noted at this site.

For M-4, if the confidence level is relaxed to the 99.0% level, 36.0% of the variation in water temperature can be accounted for by seasonality. For Dukes and Bitch of a Ditch no significant seasonal effect is noted on water temperature values which reinforces the idea of seasonal effects being well dampened by the predominantly diffuse flow and total diffuse flow nature respectively of these sites.

Correlation of log(PCO_2) against day of the year for the karst spring sites show no significant relationship exists between log(PCO_2) and sin(day) of the year, although in the case of Moons, if the significance level is relaxed to the 95.0% level, there is a positive correlation in which 12.5% of the variation can be

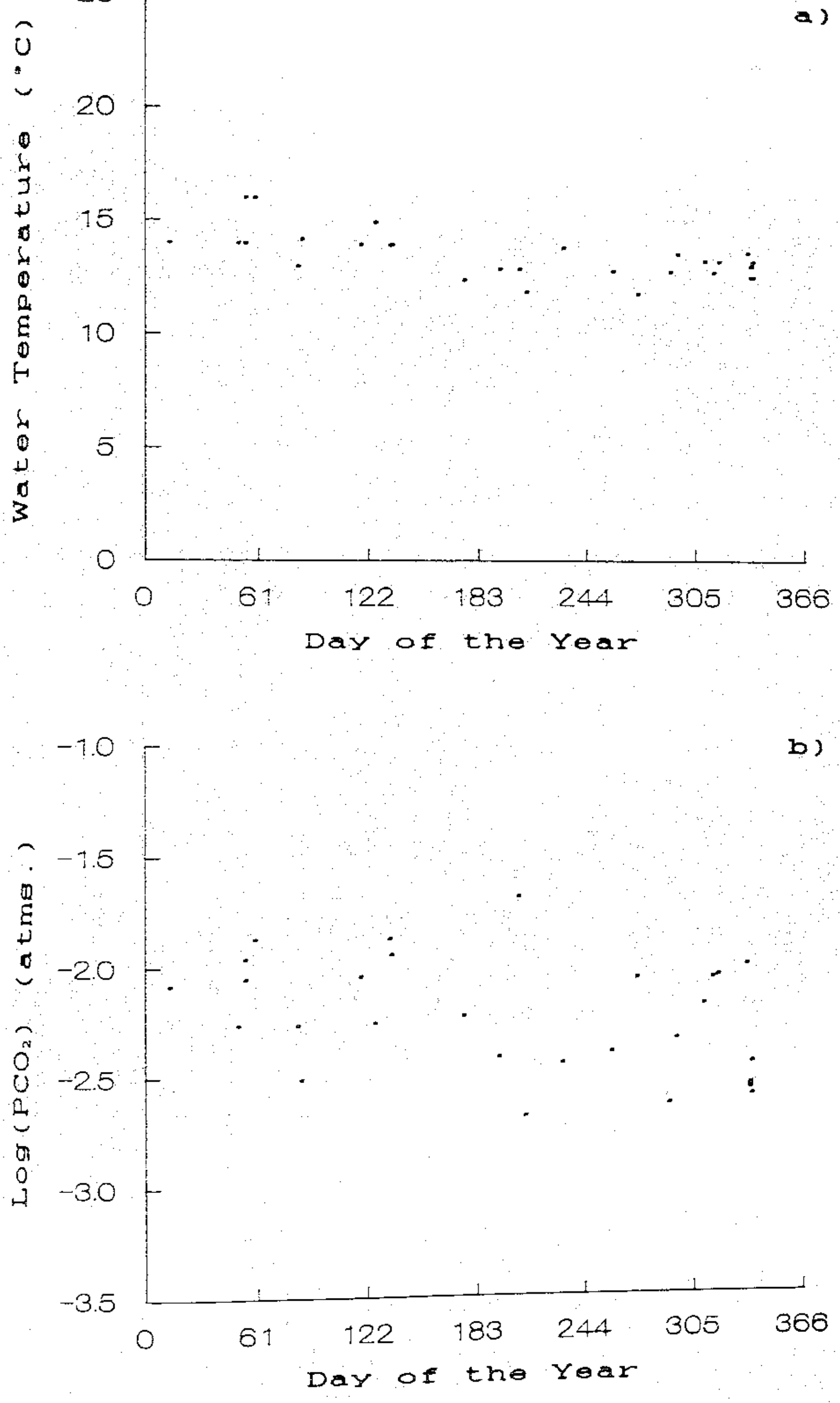


Figure 6.8. Scatterplots of a) water temperature values (°C), and b) log(PCO_2) values (atms.), against day of the year on which data was collected for Moons (an example of a mixed conduit/diffuse flow system).

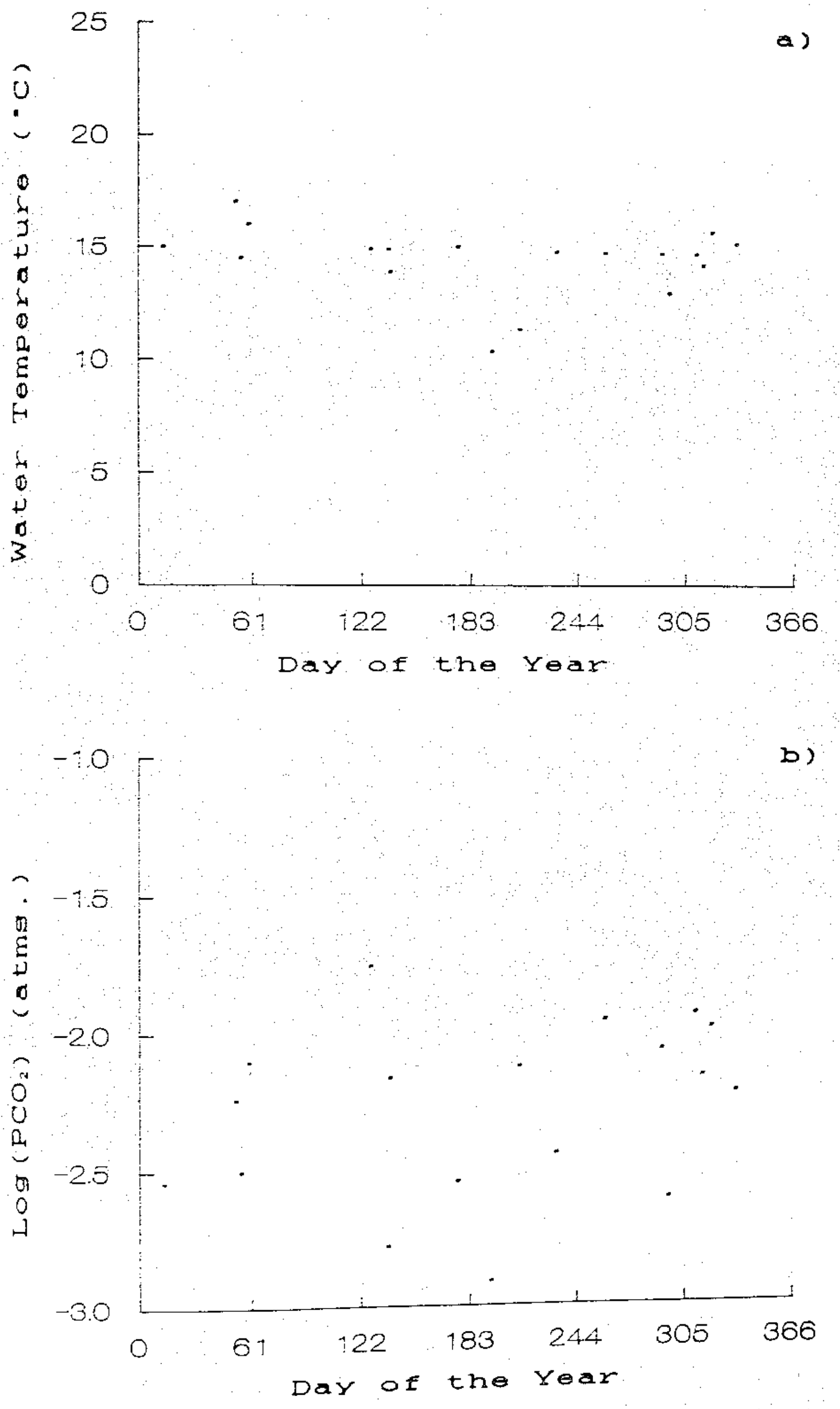


Figure 6.9. Scatterplots of a) water temperature values (°C), and b) log(PCO_2) values (atms.), against day of the year on which data was collected for M-4 (an example of a predominantly diffuse flow system with a high C_vW_T).

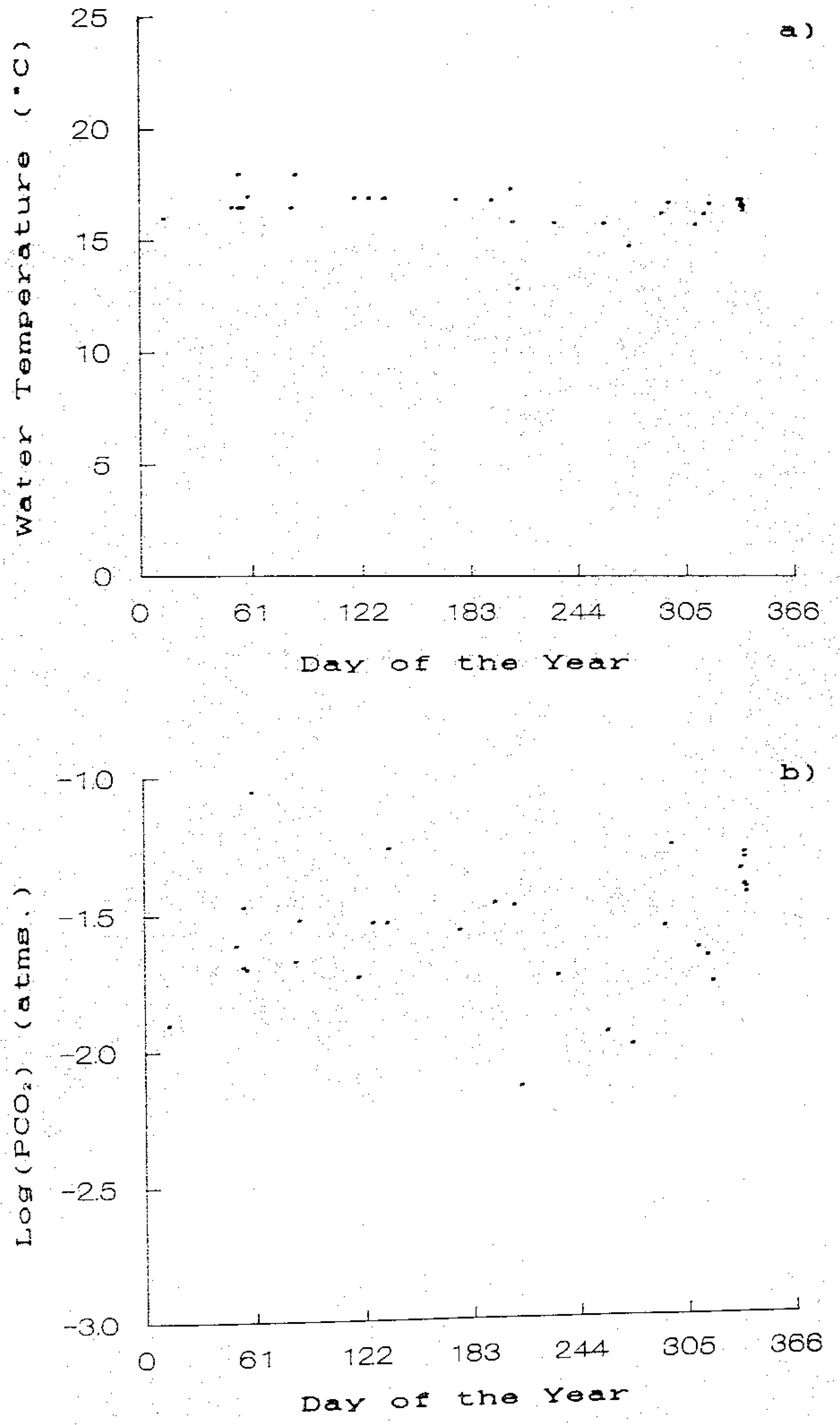


Figure 6.10. Scatterplots of a) water temperature values (°C), and b) log(PCO_2) values (atms.), against day of the year on which data was collected for Dukes (an example of a predominantly diffuse flow site with a medium C_vW_T value).

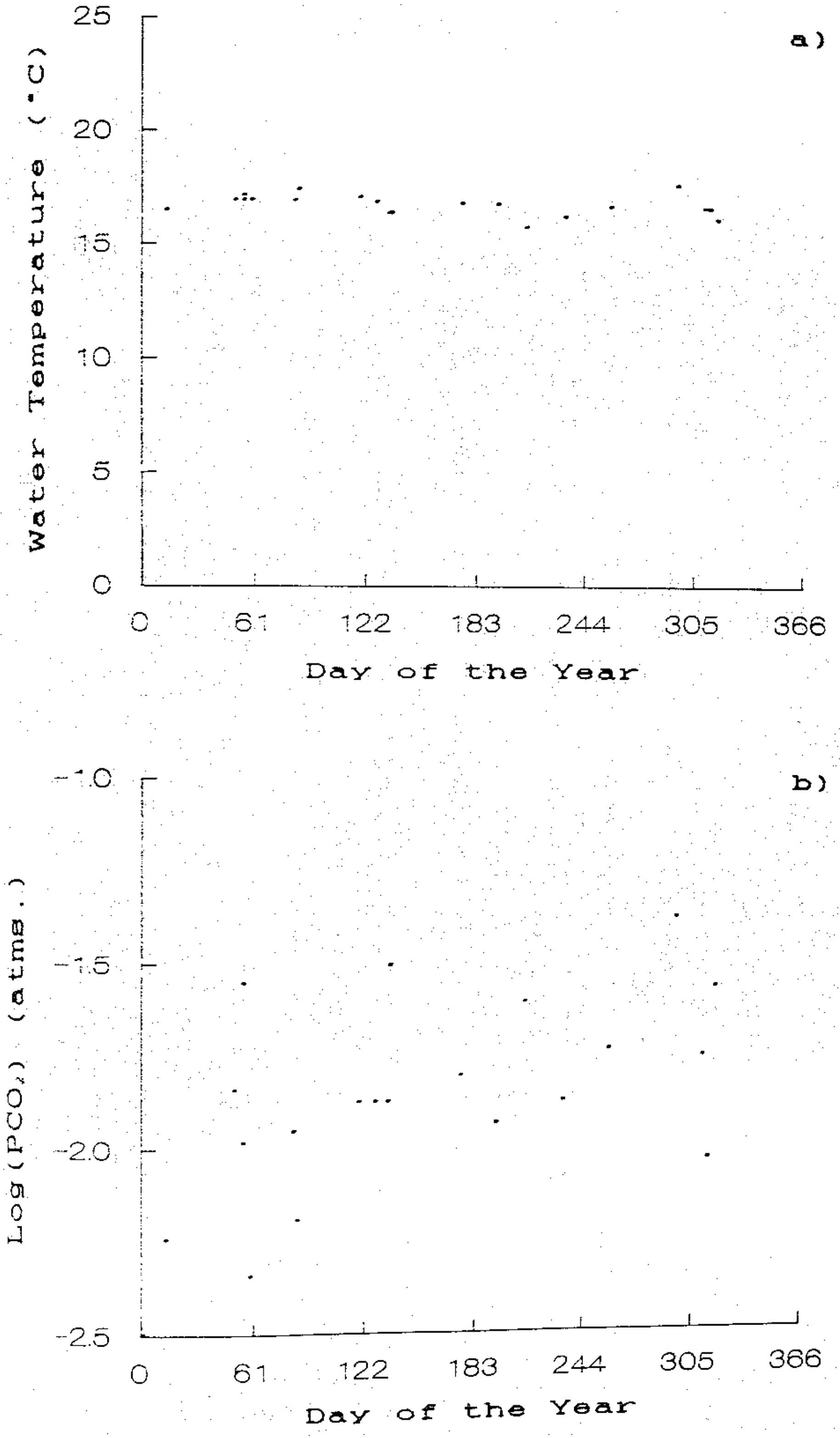


Figure 6.11. Scatterplots of a) water temperature values (°C), and b) log(PCO_2) values (atms.), against day of the year on which data was collected for Bitch of a Ditch (an example of a diffuse flow system).

accounted for by sin(day-20) indicating some seasonal influence on log(PCO_2) values at this site.

In his discussion on the seasonal variations in carbon dioxide, White notes (1988, p.210-211), " The use of karst springs as sampling points has the advantage of averaging the details that cause variations in P_{CO_2} of water following different flow paths through the aquifer. The CO_2 content of most karst water is generally independent of discharge and is not closely related to dilution and flushing out-effects. Unlike the high variability in hardness in conduit-fed springs, the calculated P_{CO_2} tends to reflect mainly the seasonal variations. Indeed smoother time curves were obtained from conduit springs than from diffuse springs. Diffuse flow springs have residence times that are long with respect to the spacing between seasonal maxima and minima; thus, P_{CO_2} calculated from the water chemistry may not keep up with the seasonal cycles".

The log(PCO_2) results obtained in this study tend to reinforce White's point, particularly so in the case of the predominantly diffuse and diffuse flow systems where any seasonal response is unable to be detected. For these sites in would appear then that, as noted by White, the residence time of recharge water is long with respect to the spacing between seasonal maxima and minima and log(PCO_2) values computed do not keep up with the seasonal cycle.

In general P_{CO_2} may be independent of discharge, but for some sites, e.g. Moons, discharge can on particular occasions greatly affect $\log(PCO_2)$ values. This is best exemplified by comparing $\log(PCO_2)$ values computed at Moons and Dukes over the four day sampling period in November-December 1987. For Dukes $\log(PCO_2)$ values were reasonably consistent over the four day period; for Moons, although $\log(PCO_2)$ values were reasonably similar on days three and four they were quite different from that noted on day one indicating that at least for this site discharge can influence $\log(PCO_2)$ values. As noted previously in this Chapter, allogenic input which exits at Moons can at a particular discharge threshold play a major role in determining spring water chemistry and hence $\log(PCO_2)$ values which are after all, computed from the raw chemical data.

SUMMARY

For the karst spring and cave water sites it has been shown in this Chapter that the variability (using coefficient of variation) of selected parameters can differ considerably between sites. The coefficient of variation of total hardness is a useful measure for distinguishing between the two spring end-members (diffuse flow and conduit flow) although one must ensure that water samples collected from each particular site are representative of the different hydrological regimes that can exist. Karst springs with C_v's of total hardness lying between the two end-member values are harder to separate and other information, in particular the saturation state of the water with respect to calcite is needed to assist in delineating spring type.

TYPE 1 water is found at the predominantly conduit flow springs when medium to high flow conditions operate. Under low flow conditions, the diffuse flow component becomes increasingly more dominant and water chemistry approaches that of TYPE 2 water.

TYPE 2 water is associated with both, mixed conduit/diffuse and predominantly diffuse flow springs and is representative of water draining predominantly limestone catchments. Under high flow conditions, storm derived recharge dominates possible components of flow; this effect is more noticable for mixed conduit/diffuse flow springs than for predominantly diffuse flow springs.

TYPE 3 water typifies diffuse flow springs with a large proportion of dolomite in their catchment.

TYPE 4 water is associated with predominantly diffuse flow systems possibly contaminated by leachate from a refuse dump.

For the the predominantly diffuse flow sites although most recharge to the respective aquifers is of a diffuse flow nature, recharge water is predominantly transported in conduits, i.e. caves. Water storage in the epikarstic zone is considered to be of prime importance in maintaining baseflow for the karst spring sites during drought conditions. The best evidence of water storage in this zone is provided by examining the physical and chemical response noted at Dukes following one particular storm event.

Seasonality would appear to have only a marginal, if any influence at all, on water temperature and log(PCO_2) values recorded for the predominantly diffuse and diffuse flow systems. For Moons (mixed conduit/diffuse flow system) seasonality does have some influence, although discharge following a storm event of a large magnitude can completely overwhelm any seasonal effect.

Models developed for karst systems in the northern hemisphere do not necessarily apply to Australian karst systems and one must be aware of a certain amount of hydrological variability inherent in the Australian landscape that does not exist in other parts of the world with the possible exception of parts of South Africa (see Finlayson et al, 1986).

CHAPTER SEVEN

CARBONATE DEPOSITION

INTRODUCTION

In previous chapters of this thesis it was noted that a number of the karst spring sites sampled record a median SI_{cal} value > 0.00 indicating supersaturation with respect to calcite. Chemical and physical results obtained from these sites, in particular the spring at Scrubby Creek, are examined in more detail in this Chapter to, i) investigate whether supersaturation with respect to calcite is a reasonable indicator of a karst spring site's ability to deposit calcium carbonate, and ii) examine possible mechanisms for calcite deposition where it is present at these sites.

TUFA OR TRAVERTINE ?

Chemical and physical studies of karst spring waters carrying a high dissolved load of carbonates which deposit $CaCO_3$ in surface streams, have been reported from many parts of the world. For example,- U.S.A.: Barnes, 1965; Herman and Lorah, 1987, 1988; Lorah and Herman, 1988; Hoffer-French and Herman, 1989; Germany: Jacobson and Usdowski, 1975; Usdowski et al, 1979; France: Dandurand et al, 1982; Canada: Wigley et al, 1973; Brook and Ford, 1982; England: Pitty, 1971;

South Africa: Marker, 1973; Yugoslavia: Emeis et al, 1987; Australia: Dunkerley, 1981, 1987; Ellaway and Finlayson, 1984; Ellaway et al, 1991.

The two main types of carbonate deposits formed are generally called either tufa or travertine although precise definitions are often not given. A number of definitions of tufa and travertine taken from various sources are given below:

> Sweeting (1973, p.335) -: tufa - soft, porous concretions of carbonate re-precipitated from saturated karst water, often around plants.
>
> travertine - regular, laminated concretions of crystalline carbonate, of similar origin to, but harder than, tufa.
>
> Jennings (1979b) -: tufa - spongy or vesicular calcium carbonate deposited from spring, river or lake waters.
>
> travertine - compact calcium carbonate deposit, often banded, precipitated from spring, river or lake water.
>
> Bögli (1980, p.184): calc-tufa - friable, porous, freshwater limestone which forms, as a rule, with contributions from assimilating plants, mostly mosses and algae.
>
> calcareous sinter - non-porous, crystalline and hard, occurring only where there are no assimilating plants.
>
> Whitten and Brooks (1983, p.66-67): calc tufa - a general name for deposits of $CaCO_3$ formed by deposition from solutions of calcium bicarbonate, $Ca(HCO_3)_2$:
>
> $Ca(HCO_3)_2 <=> CaCO_3 + H_2O + CO_2$
>
> Calc tufa is mainly found in limestone regions, filling cracks, joints, fissures, and cavities in the rocks, and around springs and resurgences of

water which have traversed limestone strata. The calc tufa formed in the cases is often spongy or cellular in character and may enclose fragments of rock, plants or animal remains. Calc tufa sometimes cements superficial gravels to produce material known as calcrete.

travertine (p.454) - a kind of calc tufa deposited by certain hot springs in volcanic regions.

Whittow (1984, p.555): tufa, calc-tufa - a sedimentary deposit formed around a calcareous spring and comprising calcium carbonate ($CaCO_3$) derived by solution of calcium bicarbonate. It is found mainly in limestone regions where it infills cavities, builds stalactites and stalagmites and cements superficial gravel to produce calcrete. In the vicinity of hot springs a type of tufa is known as travertine. Tufa is deposited when water saturated with $CaCO_3$ and CO_2 is subjected to an increase in temperature or a decrease in pressure. Loss of water by evaporation will also cause it to be deposited.

travertine (p.549) - a light coloured concretionary deposit of calcium carbonate deposited by precipitation from highly impregnated groundwater around a hot spring. It is sometimes referred to as calcareous tufa or calcareous sinter.

Hill and Forti (1986, p.197) -: only definition for travertine - calcium carbonate which is deposited from hot or cold ground water in a series of flowstone dams; specifically in caves, any flowstone or dripstone deposit.

In the context of the above definitions, the carbonate deposits found in the study area downstream of where the karst spring waters emerge are highly porous, and incorporate plant material, particularly leaves, small twigs and the roots of plants growing in the stream bed, e.g. watercress (Nasturtium officinale), as well as impurities such as detrital material, and only in the context of the deposits found in the study area will the term tufa be used.

$CaCO_3$ DEPOSITION IN SURFACE STREAMS.

Before the results and the processes or effects governing $CaCO_3$ deposition are examined it is important to, i) briefly review the chemical reactions involved, and ii) look at the method most commonly used in the literature to calculate whether or not water from a particular karst spring site is undersaturated or supersaturated with respect to calcite.

CHEMICAL REACTIONS AND SATURATION INDEX

As noted in Chapter One, the precipitation of $CaCO_3$ is best summarised by the following overall reaction,

$$Ca^{2+} + 2HCO_3^- \Longleftrightarrow CaCO_{3(solid)} + H_2O + CO_{2(gas)} \qquad (7.1)$$

Although this reaction provides an overall summary it does not really explain what the controls are that govern this reaction. From the work of Usdowski et al (1979), Dandurand et al (1982) and Hoffer-French and Herman (1989) it is noted that the above reaction (7.1) is in effect composed of two independent reactions.

When karst spring waters first appear at the surface they generally contain CO_2 concentrations much higher (in some cases up to 100 times) when compared to that of normal atmosphere, i.e. they are out of equilibrium with an atmosphere that has a log(PCO_2) value of ≈ −3.5. As a result of this disequilibrium CO_2 is given off as the system strives to establish equilibrium once again, i.e.,

$$H^+ + HCO_3^- <=> H_2CO_3 <=> CO_{2(gas)} + H_2O \tag{7.2}$$

It can be seen then that H^+ and HCO_3^- ions are lost from solution as CO_2 degases. The loss of H^+ ions from solution results in an increase in pH. As a consequence of reaction (7.2) equilibrium conditions that were established between bedrock and the groundwater under a higher PCO_2 atmosphere no longer apply and the water becomes more and more saturated with respect to calcite, i.e. further away from equilibrium, before $CaCO_3$ nucleates and begins to precipitate,

$$Ca^{2+} + CO_3^{2-} <=> CaCO_{3(solid)} \tag{7.3}$$

It must be remembered that supersaturation does not automatically lead to precipitation as nucleation of $CaCO_3$ crystals is slow and a nucleation barrier exists which must be overcome before calcite can start to precipitate. For instance Dandurand et al (1982) found that although according to a thermodynamic point of view the calcite solubility product may be exceeded (hence supersaturation), the activity of CO_3^{2-} plays a dominant role in determining whether or not calcite nucleates. They found that aCO_3^{2-} values of ≈ 22 x 10^{-6} along a karst spring fed stream needed to be exceeded before precipitation began (i.e. nucleation barrier exceeded) compared to $\approx 4.5 \times 10^{-6}$ at the spring outlet ($aCa^{2+} = 1.5 \times 10^{-3}$). Precipitation of calcite may also be inhibited by other ions and naturally occurring organic compounds found in karst spring waters either by the blocking of active growth sites or by the poisoning of prospective nucleation sites (Roques, 1969; Morse, 1983).

As noted previously (Chapter One) whether or not a particular water is supersaturated with respect to calcite, is calculated by,

$$SI_{cal} = \log.\{IAP(T^{\circ}C)/K_{cal}(T^{\circ}C)\} \qquad (7.4)$$

Briefly, IAP = ion activity product of the solution in question at temperature T°C $\{(Ca^{2+})_{aq}.(CO_3^{2-})_{aq}\}$ and K_{cal} = solubility product of calcite at temperature T°C $\{(Ca^{2+})_{eq}.(CO_3^{2-})_{eq}\}$. The values for this index indicate supersaturation for $SI_{cal} > 0.00$, equilibrium for $SI_{cal} = 0.00$, and undersaturation when $SI_{cal} < 0.00$.

TUFA DEPOSITION IN THE STUDY AREA

Of the five karst spring sites with median SI_{cal} values > 0.00 (Moons, 0.11; M-4, 0.52; Scrubby Creek, 0.54; Bitch of a Ditch, 0.62; and Dukes, 0.23) active tufa deposition is evident at all sites except Moons, with the more extensive deposits being at Scrubby Creek.

The term active tufa deposition is used here in the context that some form of tufa formation is evident in the present stream channel at each karst spring site.

Relict tufa deposits are evident at all karst spring sites except Moons, with the more extensive deposits occurring at Bitch of a Ditch. The tufa deposits at Bitch of a Ditch are now being undercut by the Buchan River with collapse of an extensive section of a tufa bank being evident (Plate 14). A U-Th date for a speleothem sample collected below the lip of the remaining relict tufa section returned a date of ≈ 2,000 years (Webb et al, in press[1]). This date indicates that this collapse feature is at least 2,000 years old with the tufa deposit being at least this old if not much greater in age. Coring of the tufa bank (using a 1m diamond tipped corer) to obtain a suitable sample for U-Th dating proved unsuccessful due to the porous nature of the deposit. Cores kept disintegrating beyond a depth of ≈ 35cm, and of the core obtained secondary calcite deposition virtually throughout the length of the core rendered it useless for dating purposes (Plate 15).

Extensive modification of the outlet at Dukes spring by the construction of a concrete swimming pool and a road is believed to have destroyed what were once quite extensive tufa deposits. Evidence of these deposits can be found, i) in the present day bed of Spring Creek just

Plate 14. Evidence of collapsed tufa bank at Bitch of a Ditch due to undercutting by the Buchan River. Present day "stream channel" and active tufa towards right hand side of photograph. Note abundance of aquatic vegetation (watercress: Nasturtium officinale) right fore-ground.

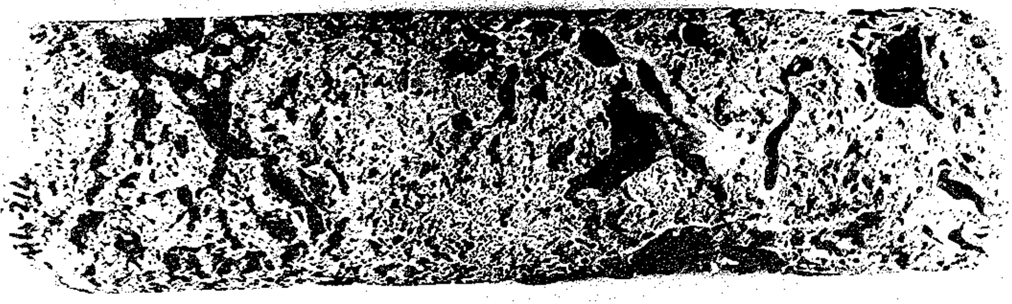


Plate 15. Core taken from the tufa bank at Bitch of a Ditch. Note highly porous nature of the deposit and evidence of secondary calcite deposition in pore spaces. Scale in centimetres and inches.

upstream of where overflow water from the swimming pool enters, and ii) about 85m further downstream is a small deposit ≈ 1.0 to 1.5m above the present stream bed of Spring Creek covered by a soil profile (Plate 16). Based on a U-Th date of ≈ 99,000 years obtained from a speleothem sample collected from the stream passage in Moons Cave (Webb et al, in press[1]) and taking into account the relative height of the stream passage in Moons and the relict soil covered tufa deposit it would appear it is > 99,000 years in age. Active tufa deposition downstream of Dukes outflow is now limited to one small area in Spring Creek (Figure 7.1 and Plate 17). Reasons for the apparent lack of contemporary active

Plate 16. Relict tufa bank now covered by soil; downstream of Dukes outflow into Spring Creek.

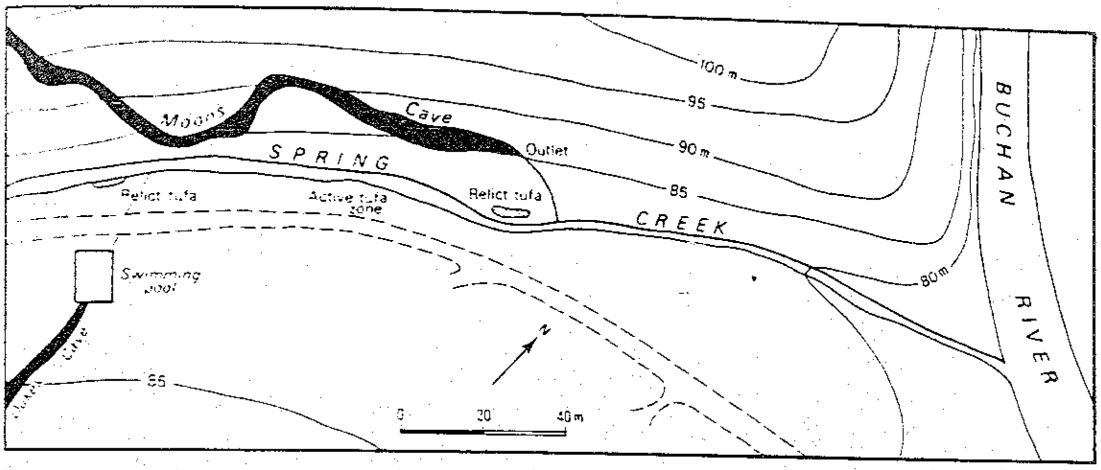


Figure 7.1. Location of active and relict tufa deposits in and along Spring Creek, Buchan Caves Reserve.

Plate 17. Site of active tufa deposition in Spring Creek downstream of Dukes outflow. Note abundance of vegetation in stream channel and scour of the bank.

tufa deposition are discussed later in this Chapter.

The phrase "relict tufa deposit" is used in the context that particular tufa deposits in the study area occupy a place in the landscape well above any possible influence of the present day karst spring waters.

Chemical analysis of the acid soluble proportion of relict (M-4, Scrubby Creek, Bitch of a Ditch and Dukes) and active (Scrubby Creek and Bitch of a Ditch) tufa deposits showed that % $CaCO_3$ ranged from 86.4% (Dukes) to 91.2% (Bitch of a Ditch) and from 97.8% (Bitch of a Ditch) to 99.1% (Scrubby Creek) respectively. % $CaCO_3$ was determined by multiplying % CaO (Table 7.1) by 1.785 [(G.F.W. $CaCO_3$) / (G.F.W. CaO)]. The data presented in Table 7.1 was obtained by the chemical analysis of a 1:200 dilution of a filtered extract of ≈ 1 gram of tufa crushed, powdered and then dissolved in a minimum amount of 1M HCl. % L.O.I. (loss on ignition) was determined by the % weight loss after ≈ 10 grams of powdered tufa sample was heated at 950°C for four hours. % acid insoluble residue was determined by the % tufa sample retained on a pre-weighed filter after acid digestion.

For both relict and active tufa deposits % $MgCO_3$ (% MgO x 2.092) is quite small in comparison to % $CaCO_3$ and only for one of the Dukes relict tufa samples is it > 1.00%. This is consistent with the limited data available in the literature regarding the chemical composition of tufa's (Irion and Muller, 1968; Pentecost, 1981; Viles and Goudie, 1990).

TABLE 7.1. CHEMICAL COMPOSITION OF OLD AND ACTIVE* TUFA SAMPLES COLLECTED FROM KARST SPRING SITES IN THE BUCHAN AREA. CHEMICAL VALUES AS % OF ACID SOLUBLE PROPORTION OF SAMPLE. % $CaCO_3$ CALCULATED FROM % CaO. L.O.I. (%) = LOSS ON IGNITION (950°C) AND INS. RES. (%) = ACID INSOLUBLE RESIDUE. [1] AND [2] DENOTE DUPLICATE ANALYSES.

SITE NO.	CaO	MgO	Fe_2O_3	Al_2O_3	K_2O	Na_2O	SiO_2	L.O.I.	$CaCO_3$	Ins. Res.
M-4[1]	49.7	0.11	0.98	3.10	<0.10	<0.10	5.41	40.7	88.7	18.4
M-4[2]	49.5	0.09	1.10	2.99	<0.10	<0.10	5.50	40.9	88.4	18.0
Scrubby* Creek	55.5	0.08	0.18	0.16	<0.10	<0.10	0.36	43.8	99.1	3.3
Scrubby Creek	50.7	0.08	0.68	1.96	0.28	<0.10	3.40	42.9	90.5	8.4
Bitch of* a Ditch	54.8	0.45	0.36	0.41	0.21	<0.10	0.60	43.2	97.8	5.4
Bitch of[1] a Ditch	50.6	0.43	1.41	1.89	0.17	<0.10	2.40	43.1	90.3	8.4
"[2]	51.1	0.46	1.54	1.84	0.22	<0.10	2.20	42.6	91.2	8.5
Dukes	48.4	0.60	3.42	2.42	0.45	<0.10	6.00	38.8	86.4	29.5
Dukes	49.0	0.32	0.74	1.98	0.63	<0.10	4.10	43.2	87.5	20.3

The % acid insoluble residue of the tufa samples analysed in this study varied considerably with higher proportions occurring in the relict tufa deposits, particularly those from M-4 and Dukes. This is not unexpected, particularly considering that the deposit near Dukes has a soil developed upon it and that both the Dukes and M-4 tufa deposits are subject to occasional inundation by floodwaters from Spring Creek and the Murrindal River respectively. Tufa samples collected from both of these sites show evidence of secondary deposition and cementation of detrital material and as such appear to be less porous than tufa now being deposited. The relict tufa deposits at Scrubby Creek and Bitch of a Ditch have notably lower acid insoluble residues than the above two sites with the most likely source being detrital material becoming trapped and being incorporated into the tufa matrix. Secondary calcite deposition is also evident in these samples particularly in the spaces left by plants that have died after being encrusted by calcite.

Irion and Müller (1968) in their study of the chemical composition of tufas from the Schwäbische Alb (Germany) found acid insoluble residues ranging from 0.0% to 9.1% with $CaCO_3$ accounting for > 99.0% of the acid soluble proportion of their samples. Viles and Goudie (1990) reported an average acid insoluble residue of 9.1% for 50 tufa samples (range 0.80% to 42.6%) from the Napier Range (north Western Australia). They found that the acid insoluble residue was predominantly silica mainly in the form of small quartz grains and cryptocrystalline material, with the most likely source being either impurities in the Napier Formation or dust derived from the surrounding area.

The two active tufa deposits analysed in this study were quite different from each other in texture and form. The Scrubby Creek sample consisted of fine crystals arranged in a filament formation and appeared to have been deposited around very fine, almost hair like, roots (Plate 18). The Bitch of a Ditch deposit consisted of coarser crystalline material deposited around watercress (Nasturtium officinale) and blackberry branches (Plate 19). It must be stressed that other forms of active tufa deposition are evident at the above two sites with a more detailed examination being needed, in particular one that looks at the influence of mosses and algae on tufa shape and form, to characterise the variety of tufa forms present (Chafetz and Folk, 1984; Pentecost and Lord, 1988).

The distance over which the present day spring waters flow from Moons, M-4, Bitch of a Ditch and Dukes before they reach a particular surface stream is quite limited (generally < 15m). M-4 and Bitch of a Ditch have surface flow for possibly 10m and 15m respectively

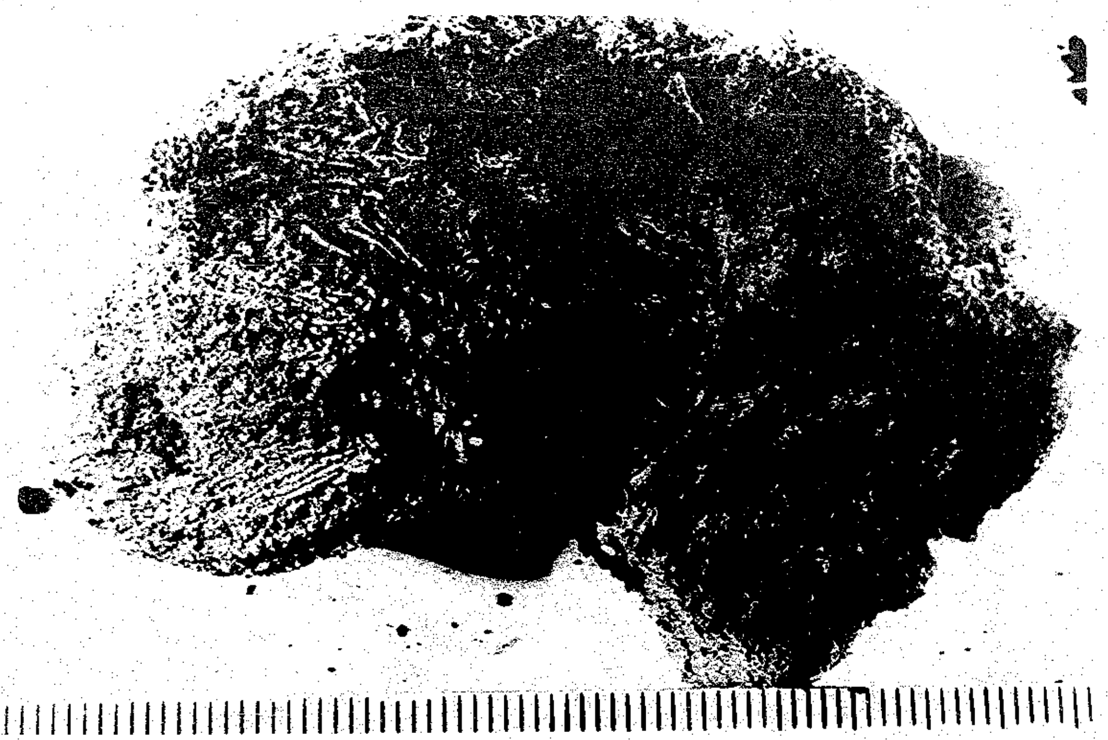


Plate 18. Photograph of a form of tufa deposited around fine root like hairs in the present stream channel at Scrubby Creek. Scale bar in millimetres.

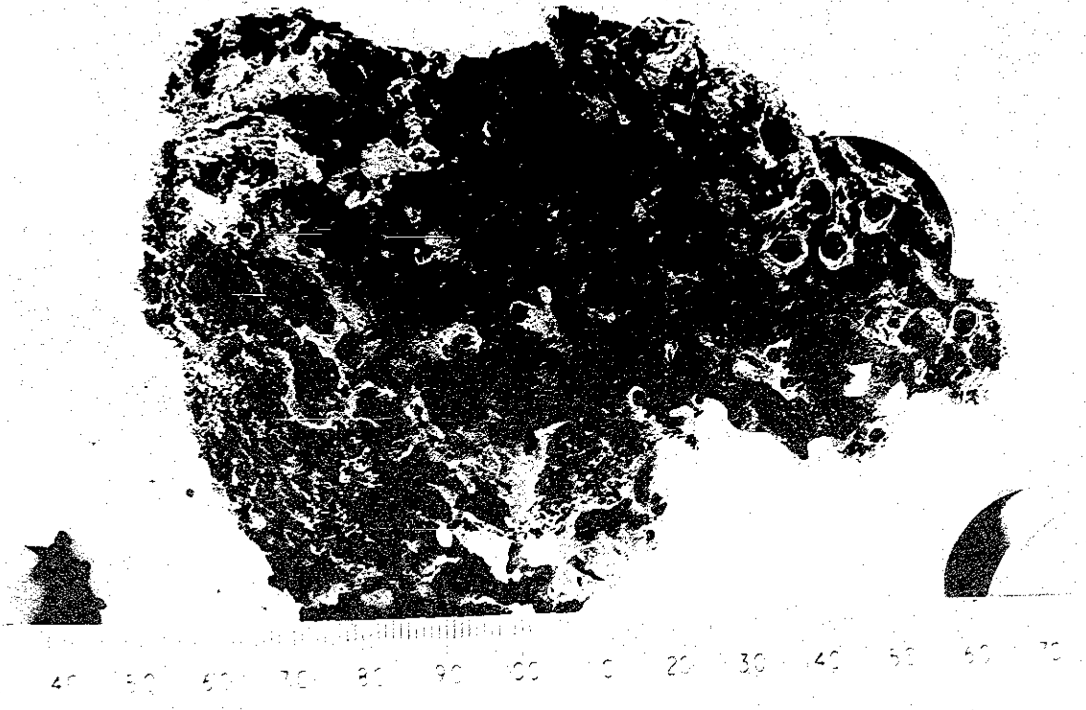


Plate 19. Active tufa deposit collected from present stream channel at Bitch of a Ditch. Scale in centimetres.

before they flow into the Murrindal River and Buchan River respectively. For Dukes the overflow from the pool is piped directly into Spring Creek, which on most occasions is usually dry upstream of this point. Spring water from Moons flows for ≈ 5m before it joins Spring Creek ≈ 80m downstream of Dukes inflow (Figure 7.1).

At the Scrubby Creek spring site, spring water flows over an extensive system of tufa terraces for a distance of ≈ 65m before it flows over a tufa waterfall and drops ≈ 4m to join Scrubby Creek. As such this site provides the best opportunity to examine possible physical and chemical changes in karst spring waters as they re-adjust to normal atmospheric conditions. As noted in Chapter Three (Table 3.1 - Site Descriptions) water samples were collected from four different locations at this site - cave water, spring water as it first emerges, spring water after it has been subjected to normal atmospheric conditions and agitation, and spring water downstream of the main zone of tufa deposition.

Median values for selected parameters for the four Scrubby Creek sites are given in Table 7.2. In general terms,

i) Ca^{2+} and HCO_3^- concentrations decrease downstream as the karst spring water degases and $CaCO_3$ precipitates (reactions (7.2) and (7.3)) whereas other ion concentrations are relatively

TABLE 7.2. MEDIAN PARAMETER VALUES FOR THE FOUR SCRUBBY CREEK SITES. ION CONCENTRATIONS AS mg/l; TOTAL HARDNESS AS mg/l $CaCO_3$; LOG(PCO_2) AS ATMOSPHERES; SI_{cal}, SI_{dol} pH AND Ca^{2+}/Mg^{2+} DIMENSIONLESS; WATER TEMPERATURE (W_T) °C.

PARAMETER	SITE 12a[1]	SITE 12b	SITE 12c	SITE 7[2]
Ca^{2+}	102.7	97.8	88.0	87.8
Mg^{2+}	7.8	7.8	7.9	7.8
Na^+	16.1	16.0	16.1	16.1
Cl^-	31.1	33.0	32.5	33.0
HCO_3^-	318.8	315.1	282.2	276.7
Log(PCO_2)	−2.06	−2.18	−2.51	−2.78
SI_{cal}	0.41	0.54	0.70	0.83
SI_{dol}	0.00	0.22	0.52	0.78
pH	7.49	7.64	7.94	8.02
W_T	16.0	16.0	16.0	15.0
Ca^{2+}/Mg^{2+}	9.65	8.09	7.25	6.85
Total Hard.	285.1	279.6	250.7	248.8
(n)	(12)	(22)	(21)	(13)

[1] Data collected 1982-1987 [2] Data collected 1985-1988

constant at all four sites,

ii) also as a result of reaction (7.2) log(PCO_2) decreases downstream as the karst spring water strives to re-establish equilibrium under new boundary conditions and CO_2 is given off,

iii) pH increases downstream as H^+ ions are lost from solution (reaction (7.2)),

iv) SI_{cal} and SI_{dol} increase downstream as the water becomes more and more saturated with respect to these minerals as the system degases at a rate greater than $CaCO_3$ or $CaMg(CO_3)_2$ can precipitate,

and, v) median Ca^{2+}/Mg^{2+} and total hardness values decrease downstream due to a loss of Ca^{2+} from solution by precipitation.

The rate of change in median parameter values such as Ca^{2+}, HCO_3^-, $\log(PCO_2)$, SI_{cal} and pH are greatest between sites 12b and 12c with only slight differences occurring between sites 12a and 12b and between 12c and site 7 (Table 7.2). It must be remembered that the data presented in Table 7.2 are median parameter values with n (the number of water samples collected) varying quite markedly and as such only general observations can be made. To get a better understanding of chemical processes or effects operating, chemical data and other results collected from all four sites on the same sampling occasion (only between May 1985 and January 1987) need to be examined.

Data presented in Table 7.3 represents three of the five occasions on which all four sites were sampled on the same occasion. The August 1986 and January 1987 data represent the minimum and maximum Ca^{2+} and HCO_3^- ion concentrations recorded over the period May 1985 to January 1987 respectively, with the May 1985 data being roughly the "average" of data recorded over this period.

Spring discharge was calculated by the salt dilution technique (Finlayson, 1979) and was ≈ 12 l/s in August 1986 and ≈ 8 l/s in May 1985 and January 1987.

Percent changes in Ca^{2+} and HCO_3^- ion concentrations and PCO_2 values between the four sample sites are given

TABLE 7.3. PARAMETER VALUES FOR THE FOUR SCRUBBY CREEK SITES SAMPLED IN MAY 1985, AUGUST 1986 AND JANUARY 1987. Ca^{2+}, Mg^{2+} AND HCO_3^- AS mg/l; Log(PCO_2) AS ATMOSPHERES; WATER TEMPERATURE (W_T) AS °C; pH, SI_{cal}, SI_{dol} AND aCO_3^{2-} DIMENSIONLESS. aCO_3^{2-} VALUES OBTAINED FROM WATSPEC COMPUTER SPECIATION PROGRAM (Wigley, 1977).

SITE NO.	Ca^{2+}	Mg^{2+}	HCO_3^-	log (PCO2)	pH	SI_{cal}	SI_{dol}	W_T	aCO_3^{2-} (10^{-6})
MAY 1985									
12a	112.0	6.3	351.7	-1.73	7.20	0.18	-0.66	16.0	4.6
12b	109.6	6.3	341.3	-2.28	7.74	0.70	0.38	16.0	15.4
12c	96.3	6.3	304.8	-2.63	8.04	0.89	0.83	16.0	26.5
7	93.0	6.3	295.9	-2.73	8.11	0.92	0.89	15.0	29.3
AUGUST 1986									
12a	93.4	8.0	314.1	-1.94	7.37	0.25	-0.35	16.5	4.2
12b	91.9	8.5	310.5	-2.32	7.74	0.59	0.37	16.0	9.4
12c	89.4	8.0	280.2	-2.76	8.12	0.89	0.95	16.0	19.6
7	85.2	8.0	275.0	-2.67	8.02	0.76	0.68	14.0	15.0
JANUARY 1987									
12a	121.3	7.7	378.0	-2.44	7.94	0.98	0.99	16.5	18.0
12b	118.9	7.6	369.5	-2.52	8.01	1.03	1.06	16.5	20.6
12c	101.2	7.4	319.0	-2.81	8.23	1.12	1.32	17.0	29.7
7	97.1	7.6	311.8	-2.72	8.14	1.03	1.15	17.5	34.8

in Table 7.4 for the above three data sets.

As noted for the data in Table 7.2 Ca^{2+} and HCO_3^- concentrations decrease downstream. For all three data sets, HCO_3^- concentrations show the greatest rate of decrease between sites 12b and 12c when compared to changes noted between sites 12a and 12b and sites 12c and 7. Ca^{2+} ion concentrations for the May 1985 and January 1987 data also show the same results. For the August 1986 data the greatest amount of Ca^{2+} change is noted to occur between sites 12c and 7. This is assumed to be simply a function of higher discharge noted on this occasion than

TABLE 7.4. % CHANGES IN Ca^{2+} AND HCO_3^- ION CONCENTRATIONS (mg/l) AND PCO_2 VALUES BETWEEN SAMPLE SITES 12a AND 12b, 12b AND 12c AND 12c AND 7.

	12a-12b	12b-12c	12c-7
MAY 1985			
δCa^{2+}	-2.0%	-12.1%	-3.4%
δHCO_3^-	-3.0%	-10.7%	-2.9%
δPCO_2	-71.9%	-55.7%	-19.7%
AUGUST 1986			
δCa^{2+}	-1.6%	-2.7%	-4.7%
δHCO_3^-	-1.1%	-9.6%	-1.8%
δPCO_2	-58.3%	-63.7%	+23.6%
JANUARY 1987			
δCa^{2+}	-2.0%	-14.9%	-4.1%
δHCO_3^-	-2.2%	-13.7%	-2.3%
δPCO_2	-16.9%	-48.7%	+23.2%

that noted for the other two data sets.

Using individual ion species molalities which take into account ion-pairs (computed by WATSPEC) and assuming one mole of Ca^{2+} reacts with two moles of HCO_3^- (reaction (7.1)), HCO_3^- is in molar excess over Ca^{2+} for all data sets between sites 12a and 12b and between sites 12b and 12c indicating that the degassing of CO_2 occurs at a faster rate than $CaCO_3$ can precipitate, this is also noted in an increase in SI_{cal} and pH values. Similar results have been noted by Barnes (1965), Jacobson and Usdowski (1975), Dunkerley (1981), Dandurand et al (1982), Brook and Ford (1982), Dunkerley (1987), Herman and Lorah (1987), Lorah and Herman (1988) and Hoffer-

French and Herman (1989) in their respective studies of tufa depositing karst spring waters.

Between sites 12c and 7 for the August 1986 and January 1987 data, changes in Ca^{2+} ion concentrations are in molar excess over HCO_3^- changes indicating that between these two sample sites $CaCO_3$ is precipitating at a faster rate than CO_2 degassing. For the May 1985 data, molar changes in Ca^{2+} ion concentration are almost balanced by molar changes in HCO_3^- ion concentration indicating that CO_2 degassing and $CaCO_3$ precipitation are occurring at approximately the same rate.

For the May 1985 data a SI_{cal} value > 0.70 and a aCO_3^{2-} value $> 15.4 \times 10^{-6}$ would appear to have been necessary before significant amounts of $CaCO_3$ precipitated. For the January 1987 data a SI_{cal} value > 1.03 and a aCO_3^{2-} value $> 20.6 \times 10^{-6}$ are needed before significant amounts of $CaCO_3$ precipitate which are similar to results reported in the literature. Usdowski et al (1979) noted that spring water needed to reach about 12 times saturation ($SI_{cal} \approx 1.08$) with an aCO_3^{2-} value $\approx 29 \times 10^{-6}$ for $CaCO_3$ deposition. Dandurand et al (1982) noted that five to ten times supersaturation (SI_{cal} 0.69 to 1.00) and aCO_3^{2-} value $\approx 22 \times 10^{-6}$ was needed before significant $CaCO_3$ deposition occurred. This increase in aCO_3^{2-} values is caused by an increase in pH due to CO_2 degassing (reaction (7.2)). Herman and Lorah

(1988) in their study noted that values of up to fifteen times supersaturation were recorded (SI_{cal} ≈ 1.18) where water turbulence was considerable which caused a rapid flux of CO_2 degassing, which also corresponded with a zone of significant $CaCO_3$ deposition.

Spring waters which emerge supersaturated have also been reported by Jacobson and Usdowski (1975), Dunkerley (1981) and Ellaway et al (1991). In other studies, spring water at emergence has been reported as just undersaturated (Brook and Ford, 1982; Dandurand et al, 1982; Hoffer-French and Herman, 1989) or just saturated with respect to calcite (Barnes, 1965; Dunkerley, 1987) and needs to flow, in some cases up to a 1km (Lorah and Herman, 1988) before a significant level of supersaturation is achieved and $CaCO_3$ deposition takes place. As noted previously supersaturation does not necessarily imply $CaCO_3$ precipitation (Suarez, 1983; Troester and White, 1986; Emeis et al, 1987). For example Emeis et al (1987) found that although SI_{cal} values of 0.53 to 0.78 were observed in fast moving streams draining carbonate rocks no evidence of $CaCO_3$ deposition in these streams was found.

So far in this section only chemical effects have been looked at to explain the depletion in Ca^{2+} and HCO_3^- ion concentrations downstream of the spring, other controls noted in the literature will now be considered to see if they play any role, major or minor, in influencing $CaCO_3$ deposition at Scrubby Creek. Data collected from the other karst spring sites will also be examined.

CONTROLS ON CALCITE DEPOSITION

According to Ford (1989) the controlling factors on $CaCO_3$ deposition are,

i) supersaturation with respect to calcite,
ii) water temperatures generally > 12.0 C,
iii) turbulence,
iv) low dissolved organic carbon content,
v) presence of blue-green algae (cyanobacteria),
and vi) loss of CO_2 by cooling (thermal waters only).

To those controls listed above Dunkerley (1987, 1988) found that evaporation was also a significant factor in tufa deposition, particularly in a seasonally arid area, and should be taken into account.

The processes involved can, for convenience, be divided into an inorganic and an organic component. Inorganic effects are solely related to the degassing of CO_2 from karst spring waters as they re-adjust to normal atmospheric conditions with the associated chemical and kinetic effects, i.e. the chemical reactions involved and the rate at which these reactions occur. Also included above should be any chemical changes bought about by changes in physical parameters such as water temperature, turbulence, evaporation, etc.

Organic processes are more controversial and are mainly attributed to either CO_2 uptake due to the metabolic activity of micro-organisms (cyanobacteria-blue green algae) or to the assimilation of CO_2 by lower order plants. Whether the trapping of minute calcite crystals or the role of plants as a substrate for calcite nucleation can be termed "organic processes" or not is extremely difficult to determine. For convenience these processes are grouped together under a broad heading of organic processes.

Barnes (1965) in his study of a travertine depositing stream in an arid area of California found that calcite precipitation was closely associated with plants, but superimposed on these biologic effects were the inorganic effects brought about by CO_2 degassing and increases in water temperatures. He noted that water became increasingly saturated with respect to calcite in a downstream direction as the rate of CO_2 loss exceeded the rate of calcite precipitation. The role of evaporation in aiding increased saturation (due to water loss) he noted was minimal. He found that S_{cal} values of 3.3 to 4.1 (i.e. SI_{cal} values of 0.52 to 0.61) were perhaps needed before calcite deposition could begin and that perhaps vegetation surfaces acted as nucleation sites.

Pitty (1971) in his study of tufa deposition at Goredale Scar found that seasonal responses of plant activity could influence tufa deposition by metabolic processes. On the other hand studies by Usdowski et al (1979), on a calcite depositing stream in Germany, and Dandurand et al (1982) on a calcite depositing stream in France, found that metabolic effects were negligible in systems with high supply rates of dissolved carbonate species. In both these studies variations in major ion components and the isotopic fractionation of ^{13}C and ^{18}O over a diurnal cycle were within the errors of determination and as such negligible changes were noted.

Emeis et al (1987) in their examination of travertine formation in Plitvice National Park found that calcite deposition was closely related to biogenic factors. They found that three pre-requisites needed to be satisfied before $CaCO_3$ precipitation would take place. They were,

i) calcite supersaturation,

ii) presence of calcite seed crystals,

iii) biological activity.

They considered the loss of CO_2 from solution by biological activity (hence increased supersaturation) was minimal, what they found was that algae and mosses provided a substrate that either trapped calcite particles or provided fresh growth sites for calcite.

Hoffer-French and Herman (1989) in their study of the hydrological and biological influences on CO_2 degassing found that the concentration gradient between dissolved CO_2 in the stream water and that of the partial pressure in the atmosphere was sufficiently steep that biological effects on CO_2 degassing were minimal.

Marker (1973), Dunkerley (1981), Dandurand et al (1982), Herman and Lorah (1987) and Lorah and Herman (1988) found that turbulence was the main driving force behind CO_2 degassing and calcite precipitation in their studies of tufa depositing streams. They all noted that turbulence increases the surface area of solution exposed to the atmosphere which in turn allows a higher rate of CO_2 degassing to occur at the gas-liquid interface (reaction (7.2)). Roques (1969) found similar results in laboratory studies in that nucleation of $CaCO_3$ increased as the stirring rate of a supersaturated solution increased.

At Scrubby Creek turbulence appears to be the main driving force behind tufa deposition particularly between sites 12b and 12c in that it enhances CO_2 degassing. For systems with high supply rates of dissolved carbonate species ranging from 1.2g HCO_3^-/s (Jacobson and Usdowski, 1975) to ≈ 25g HCO_3^-/s (Dandurand et al, 1982) to 101g HCO_3^-/s (Lorah and Herman, 1988) metabolic effects have been shown to be negligible. Using the median HCO_3^- value for site 12b and assuming an average discharge value of 8 l/s a supply rate of 2.5g HCO_3^-/s is obtained for Scrubby Creek which fits in with the above data.

As noted at the start of this Chapter tufa deposition in the study area occurs predominantly in association with either living or dead plant material (Plate 20) and it would appear that it plays a major role by either trapping minute calcite crystals and hence enhancing calcite growth sites or by providing a substrate for nucleation sites (Barnes, 1965; Brook and Ford, 1982; Emeis et al, 1987; Herman and Lorah, 1988).

As noted previously in this Chapter, active tufa deposition is evident at three other karst spring sites in the study area (M-4, Bitch of a Ditch and Dukes). For both M-4 and Bitch of a Ditch active tufa deposition is evident immediately downstream of the point of emergence. This is assumed to indicate that although discharge and turbulence are notably less than that observed at Scrubby Creek (discharge generally between 0.0 and 1.0 l/s and between 0.2 and 0.5 l/s for M-4 and Bitch of a Ditch respectively) a sufficient gradient

Plate 20. Incorporation of both live and dead plant material into tufa matrix in pool of shallow water at Scrubby Creek.

still exists between $CO_{2(aq)}$ and $CO_{2(air)}$ to enable rapid degassing of CO_2 to occur. Watercress (Nasturtium officinale) is abundant in the "stream channel" at both sites and often obscures any evidence of flow. It would appear that the presence of watercress, due to the tufa forms found, plays an important role in tufa deposition at both these sites. Whether this is mainly due to metabolic processes or a restriction on flow that enables a given body of water more time to degas or the presence of a substrate for calcite growth sites is hard to determine but most likely is a combination of all three processes (Ford, 1989).

Based on chemical data collected from Dukes spring and a site in Spring Creek below where active tufa deposition is evident, significant changes in Ca^{2+} ion concentration downstream indicating $CaCO_3$ deposition were recorded on only one out of three occasions (Table 7.5). One possible reason for this now apparent lack of tufa activity could be due to a change in the chemistry of water now discharging at Dukes from that in the past.

TABLE 7.5. SELECT PARAMETER VALUES FOR DUKES (a) AND A SITE IN SPRING CREEK BELOW WHERE ACTIVE TUFA DEPOSITION OCCURS (b). ION CONCENTRATIONS IN mg/l; LOG(PCO_2) AS ATMOSPHERES; SI_{cal} AND pH DIMENSIONLESS.

	Feb. 1985		Nov. 1987		March 1988	
	a)	b)	a)	b)	a)	b)
Ca^{2+}	160.0	148.6	144.3	143.5	171.8	168.4
Mg^{2+}	28.9	26.8	29.4	28.4	35.1	34.3
Cl^-	203.9	195.7	206.0	208.0	236.5	235.6
$\log(PCO_2)$	-1.61	-2.37	-1.34	-1.99	-1.52	-2.03
SI_{cal}	0.34	1.03	0.03	0.66	0.37	0.83
pH	7.17	7.91	6.89	7.54	7.12	7.16
HCO_3^-	446.2	431.5	429.6	420.6	483.9	459.3

As noted previously in this thesis water discharging at Dukes has been traced to water from B-67, which in Chapter Five was assumed to have been contaminated by leachate from a refuse dump. Possible effects could be that calcite growth sites are being poisoned or blocked by particular inorganic elements and organic compounds present in the leachate causing inhibition of $CaCO_3$ deposition. Another possible reason for this apparent lack of tufa activity could be that the construction of the swimming pool and road have greatly altered flow characteristics of the spring water from Dukes, which obviously will affect degassing rates. Flash floods in Spring Creek will also play a part in limiting tufa build up in that under high discharges scour of the bank and stream channel occurs.

The lack of evidence of tufa deposition at Moons is primarily attributed to its mixed conduit/diffuse flow behaviour, which in turn influences spring water temperature and secondly to the very short distance (< 5m) the spring water flows before it joins Spring Creek. The short distance travelled means that there is very little time for the discharging spring water to reach a sufficient level of supersaturation before calcite deposition will take place.

Moons records the lowest median water temperature (13.5°C) of the five karst springs with median SI_{cal} values > 0.00 and is only marginally warmer than the minimum value of 12.0°C noted by Ford (1989) as being one of the controlling factors behind tufa deposition whereas median water temperature values range from 15.0 to 17.0°C at the other karst spring sites.

The flow characteristics of each karst spring i.e. where it lies along the diffuse-conduit flow continuum, is considered to be a major factor, at least for the karst springs at Buchan, in determining whether or not tufa deposition takes place at a particular karst spring site. This is reinforced by the fact that the karst spring sites with the most notable tufa deposits (Bitch of a Ditch, Scrubby Creek and M-4) are diffuse to predominantly flow systems respectively which are highly supersaturated with respect to calcite on almost all occasions i.e. $SI_{cal} > 0.50$ where spring water first emerges, whereas at Moons conduit flow behaviour and undersaturation with respect to calcite is much more evident. The diffuse/predominantly diffuse flow nature of the aquifers means that an almost constant and regular supply of water supersaturated with respect to calcite exists, and this provides a situation ideally suited for calcite deposition.

SUMMARY

The most notable tufa deposits (relict and active) found in the study area occur at diffuse/predominantly diffuse flow karst spring sites, in particular Bitch of Ditch and Scrubby Creek. This is primarily attributed to the practically constant and regular supply of water supersaturated with respect to calcite. Inorganic and organic mechanisms or processes determine where and what form or variety of calcite deposition takes place. The relative importance of inorganic and organic mechanisms varies from site to site and also varies considerably from place to place at each site. Where water flow is turbulent inorganic processes will generally dominate due to an increase in the degassing rate. In quieter sections or where flow is reduced organic processes are assumed to dominate due to the proliferation of particular water plants.

Karst spring sites need to be sampled over a range of hydrological conditions before a reasonable estimate can be made of a site's ability to deposit calcium carbonate and a median SI_{cal} value > 0.50 would appear to be necessary, at least in this study area.

CHAPTER EIGHT

CONCLUSION

The results obtained and presented in this thesis show the importance of such studies in identifying the controls and processes that can operate in karst areas. This is particularly so for small impounded karst areas in southeastern Australia for which very little information is available concerning the hydrochemical characteristics of carbonate waters present.

Principally, four distinct water types and four distinct flow types are found to be associated with the karst spring and cave water sites sampled in this study.

A subjective classification was used to separate the sites into groups on the basis of physical and chemical characteristics of the water. Cluster analysis also confirmed the appropriateness of this grouping of sites.

The spatial variation observed for particular median parameter values (e.g. water temperature, Ca^{2+}, Mg^{2+}, Cl^- and Ca^{2+}/Mg^{2+} molar ratio) is considerable. The spatial variability noted for three of the four water types found (TYPES 1, 2 and 3) is controlled by intrinsic factors. Particular aspects of catchment lithology, residence time of recharge, slope aspect and vegetation cover are "in-built" into each system and are the major factors that control and determine the physical and chemical characteristics noted.

Sites with TYPE 4 water, as well as being controlled by intrinsic factors (as for the above three water types) are also possibly affected by contamination by leachate from a refuse dump. Hence although four water types are found, only three water types are in fact considered to be representative of "**natural**" carbonate waters found in the study area.

The co-efficient of variation of two particular parameters, notably total hardness (Cv.Tothd.) and water temperature (C_vW_T), used in conjunction with the median SI_{cal} value are suggested as being the minimum number of variables required for an reasonable assessment of flow type to be achieved; in some cases further information may be required to delineate flow types. A C_vTothd. value of ≈ 25% was found to be useful in distinguishing between sites with mixed conduit/diffuse flow and sites with predominantly diffuse flow systems, in particular for karst spring sites with median SI_{cal} values > 0.00. A C_vW_T value of ≈ 10% allows for a distinction to be made between predominantly conduit flow systems and surface waters with similar median parameter values and similar C_vTothd.. Median SI_{cal} values < 0.00 are taken to generally indicate predominantly conduit flow systems, with median SI_{cal} values > 0.00 indicating flow systems lying between the mixed conduit/diffuse flow and diffuse flow end members.

A summary of water and flow types found in the study area for the karst spring and cave water sites with general observations are given in Table 8.1.

The co-efficient of variation of total hardness value used in this study to differentiate between mixed conduit/diffuse and predominantly diffuse flow systems is notably higher than that suggested by Shuster and White (1971; 1972) as being useful to distinguish between conduit and diffuse flow systems (≈ 10%). This is believed to be due to the fact that Australian hydrologic systems, in particular those in southeastern Australia have an unusually high variability by world standards.

This inherent variability has best been demonstrated when stream discharge and runoff variability for Australian systems are compared with data obtained from different parts of the world (McMahon, 1982; Finlayson et al, 1986; McMahon et al, 1987; Finlayson and McMahon, 1988; Kuhnel et al, 1990). Kuhnel et al (1990) in their recent study found that the higher rainfall variability, hence higher runoff variability associated with southeastern Australia streams (when compared to those from southeastern U.S.A.), could be partly explained by rainfall patterns associated with the El Nino-Southern

TABLE 8.1. SUMMARY OF FLOW AND WATER TYPES ASSOCIATED WITH THE KARST SPRING AND CAVE WATER SITES WITH GENERAL OBSERVATIONS.

FLOW TYPE	WATER TYPE	GENERAL OBSERVATIONS
Predominantly conduit flow	TYPE 1	Median chemical values similar to those generally observed for major and minor surface streams with predominantly non-carbonate catchments. Co-efficient of variation values for Ca^{2+}, Mg^{2+}, HCO_3^- and total hardness similar to those observed for surface stream sites with carbonate catchments. Water is generally undersaturated with respect to calcite and dolomite (as observed for surface streams with non-carbonate catchments) but is easily distinguishable from surface waters by low C_vW_T values ($\approx \leq 10\%$).
Mixed conduit/diffuse flow	TYPE 2	Median chemical values closer to those observed for the predominantly diffuse flow sites with TYPE 2 water. Readily distinguishable by high co-efficient of variation values for Ca^{2+}, Mg^{2+}, HCO_3^- and total hardness from other flow systems with TYPE 2 water (C_v values for the above four parameters more similar to those noted for the predominantly conduit flow systems and also surface stream sites with carbonate catchments). Water supersaturated with respect to calcite on 62% of occasions sampled; no evidence of relict or active tufa deposition. Notably cooler than water types 3 and 4.

TABLE 8.1 (CONT.)

FLOW TYPE	WATER TYPE	GENERAL OBSERVATIONS
Predominantly diffuse flow	TYPE 2	Median chemical values obtained assumed to be characteristic of of sites sampled in the study area with catchments predominantly of limestone. Only undersaturated with respect to calcite (and dolomite) after high flow events of a particular magnitude. Median $SI_{cal} > 0.50$; extensive tufa deposits.
Predominantly diffuse flow	TYPE 4	Generally highest median chemical parameter values recorded, particular for Na^+ and Cl^- which possibly indicate contamination. Only undersaturated with respect to calcite (and dolomite) after high flow event of particular magnitude.
Diffuse flow	TYPE 3	Median chemical values associated with sites with predominantly dolomite catchments. Supersaturated with respect to calcite no matter what flow regime is operative. Median $SI_{cal} > 0.50$; extensive tufa deposits. Lowest co-efficient of variation values for water temperature and total hardness.

Oscillation (ENSO) phenomenon.

The effect of the ENSO phenomenon (with a 28 to 85 month oscillation signal) shows how important it is for sites to be sampled over considerable periods of time and for samples to be collected over the whole range of hydrological regimes that can exist within a particular study area. As discussed in Chapter Six, the difference noted in the co-efficient of variation values for two sites (B-67 and B-41) that have almost identical median parameter values (and are assumed to represent the same body of groundwater) is due simply to the time period over which data was obtained.

Karst spring sites at which the largest tufa deposits (both relict and active) occur in the study area are associated with diffuse to predominantly diffuse flow systems that record a median $SI_{cal} > 0.50$. Inorganic processes control tufa deposition where turbulent flow occurs due to higher degassing rates, whereas organic processes dominate where flow is retarded and aquatic vegetation such as watercress (Nasturtium officinale) thrives.

In conclusion, the data presented in this thesis gives a reasonable assessment of the hydrochemical characteristics of a small impounded karst area in southeastern Australia. The installation of continuous recording devices for a number of parameters (e.g. stage, water temperature, air temperature and conductivity) at each of the karst spring sites is needed to elucidate residence times of recharge, the mixing of old prestorm water and new storm water, the influence of slope aspect on groundwater temperature and the relationship between mean annual air temperature and groundwater temperatures, before the hydrological and chemical processes operating at each site can be fully understood.

Although not a major part of this thesis the possible contamination of groundwater by leachate from the refuse dump is of particular concern and highlights potential or existing problems associated when such sites are located in or near carbonate terrains. The problem of possible contamination at Buchan is further excaberated by the fact that water at Dukes spring is used to maintain, without prior treatment, a swimming pool for the public within the Buchan Caves Reserve and is also used as a water supply to wash calcite formations in the two main tourist caves at Buchan.

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APPENDIX A.

IN-SITU FIELD MEASUREMENTS AND RESULTS OF CHEMICAL ANALYSES FOR ALL SITES SAMPLED. Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-} AND SO_4^{2-} AS mg/l; ALKALINITY (ALK.) AS mg/l $CaCO_3$; pH DIMENSIONLESS; Eh (mV); CONDUCTIVITY (COND) µS cm⁻¹, 25.0°C; WATER TEMPERATURE (W_T) °C.

YEAR	DAY	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Cl^{-}	ALK.	SO_4^{2-}	pH	Eh	COND	W_T
SITE 1 (BUCHAN RIVER)												
1982	295	9.0	2.5	5.5	0.7	8.0	27.5	3.7	7.73	504	92	14.5
1983	54	70.1	14.7	26.5	1.9	60.0	207.2	.	8.11	412	600	21.5
1983	310	7.6	2.6	5.1	0.7	8.0	29.5	2.1	7.54	407	94	18.0
1984	59	14.4	4.2	8.8	1.8	14.0	49.5	3.7	6.86	391	231	20.5
1984	135	6.2	2.5	5.9	1.6	8.0	29.0	<0.5	7.04	439	.	10.5
1984	210	2.9	1.7	6.3	1.7	7.0	22.3	<0.5	7.38	407	.	9.0
1984	259	2.6	1.5	5.8	0.9	6.0	19.9	<0.5	7.50	443	68	10.0
1984	318	7.1	2.8	8.7	1.8	5.6	38.2	3.7	7.51	396	100	18.0
1985	50	22.1	5.8	13.3	2.7	21.8	78.0	1.1	7.70	.	198	20.0
1985	126	11.5	2.8	14.5	1.6	13.6	48.1	.	7.30	.	144	14.0
1986	175	7.9	2.5	7.8	0.9	6.0	40.5	2.9	7.35	428	174	9.0
1986	233	2.4	1.2	6.0	0.9	6.1	21.2	.	8.16	462	59	9.0
1986	291	3.2	1.5	3.5	1.0	4.0	17.2	.	7.91	419	54	14.0
1986	314	6.5	2.7	4.0	1.0	5.5	31.4	.	7.79	.	62	17.0
1987	13	6.0	2.8	5.5	1.2	7.0	29.6	.	8.01	420	83	20.0
1987	55	6.8	3.4	7.4	1.6	9.0	34.6	.	7.55	391	98	21.5
1987	83	8.0	3.5	7.0	1.2	8.0	38.9	.	7.59	429	110	14.5
1987	118	8.0	3.2	9.0	1.6	11.0	41.4	.	7.39	425	113	16.0
1987	134	21.2	16.5	29.9	5.4	68.4	101.0	.	7.39	398	460	13.0
1987	195	5.5	2.6	5.4	0.7	6.5	30.0	.	7.38	.	78	7.0
SITE 2 (MURRINDAL RIVER)												
1982	297	18.9	11.3	16.9	1.8	36.0	70.1	6.0	7.50	430	271	14.0
1983	55	54.7	16.5	23.8	2.3	43.0	194.8	.	8.18	361	522	31.0
1983	313	19.4	6.8	9.9	1.5	22.0	73.7	3.8	7.58	416	246	20.0
1984	59	32.0	10.1	17.1	3.6	29.0	115.0	4.2	7.51	391	302	20.0
1984	137	25.9	11.2	16.9	2.6	35.0	102.3	4.0	7.05	435	398	10.0
1984	211	3.9	1.4	7.9	2.5	10.0	20.8	.	7.32	411	.	10.0
1984	319	16.2	8.0	20.5	3.8	33.9	80.8	.	7.49	409	254	17.0
1985	52	20.5	6.9	14.9	4.7	30.4	72.0	2.9	7.76	.	262	26.0
1985	127	19.0	11.5	16.2	4.3	39.1	85.3	.	7.54	.	435	11.0
1986	176	20.2	11.5	15.5	2.3	34.1	81.9	.	7.91	440	240	6.0
1986	232	21.0	11.3	16.7	2.1	41.3	76.8	.	7.39	435	280	11.5
1986	315	20.5	8.1	14.3	3.2	32.9	76.4	.	7.20	.	270	18.0
1987	13	17.8	8.5	16.1	3.0	31.0	72.2	.	7.62	416	356	22.0
1987	55	29.9	8.7	17.1	4.3	31.0	110.8	.	7.51	398	266	18.0
1987	119	16.5	6.8	15.2	2.7	27.0	64.2	.	7.33	.	224	13.5
1987	134	19.5	6.8	14.7	3.2	31.9	65.8	.	7.02	415	236	14.5
1987	195	28.3	13.7	19.1	2.0	46.2	108.3	.	7.93	.	310	9.0
1987	334	23.7	9.9	17.9	2.3	35.0	87.0	.	7.27	.	283	21.5
1988	87	20.0	7.6	17.3	2.8	29.2	80.9	.	7.61	.	269	19.3

YEAR	DAY	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Cl^{-}	ALK.	SO_4^{2-}	pH	Eh	COND	W_T
SITE 3 (SNOWY RIVER)												
1982	296	11.0	5.7	9.1	0.7	14.0	48.2	1.2	7.80	401	135	16.0
1983	55	11.5	9.1	14.2	2.1	23.0	67.8	.	8.15	386	218	24.0
1983	313	8.5	6.5	8.1	0.9	13.0	46.3	4.3	7.63	397	151	22.0
1984	60	10.4	8.4	12.9	1.7	19.0	67.0	3.1	7.44	398	209	21.0
1984	137	7.8	5.7	10.0	1.3	16.0	46.4	1.0	7.38	459	159	11.0
1984	211	6.3	3.7	13.2	1.9	18.0	36.0	.	7.85	399	.	12.0
1984	259	4.6	5.2	10.4	1.5	13.0	35.1	.	7.53	436	138	13.5
1984	318	8.2	8.1	14.3	1.8	16.7	57.0	4.3	8.14	402	185	21.5
1985	52	10.4	9.2	15.3	2.3	21.8	68.5	.	8.53	.	211	23.0
1985	131	12.0	8.9	16.7	2.0	27.6	68.7	.	7.97	.	245	14.0
SITE 4 (SPRING CREEK)												
1982	295	17.7	14.9	27.3	2.7	50.0	78.6	9.1	7.05	457	338	12.0
1983	54	91.2	29.9	41.7	10.3	82.0	333.7	.	7.10	381	851	19.0
1983	310	7.9	6.9	19.5	2.0	32.3	52.0	2.1	7.39	423	230	14.5
1984	59	11.6	11.5	28.3	7.3	58.0	60.4	10.4	6.96	412	308	16.0
1984	135	13.6	12.9	32.2	4.6	74.0	60.5	2.5	6.82	423	363	9.0
1984	210	4.7	2.1	13.6	2.5	14.0	30.0	<0.5	7.38	422	.	9.0
1984	259	3.0	3.5	18.2	2.3	25.0	28.4	<0.5	7.50	438	149	10.0
1984	318	8.8	8.2	25.3	5.9	40.6	57.3	3.9	7.63	408	328	15.0
1986	175	19.5	11.9	27.4	4.5	66.5	70.1	4.2	7.45	438	330	8.0
1986	231	22.6	18.6	47.0	4.4	114.9	83.2	8.6	7.49	436	522	9.0
1986	291	13.6	11.4	31.2	5.1	62.9	63.9	.	7.65	413	335	12.0
1986	315	45.8	15.4	31.1	2.0	71.2	155.1	.	7.80	.	568	14.0
1987	13	21.2	14.6	31.8	4.5	62.0	107.7	.	7.79	403	444	14.5
1987	54	12.6	10.0	16.8	4.9	49.0	49.1	.	7.37	412	300	15.5
1987	83	37.8	13.9	28.7	4.8	65.0	139.8	.	7.46	429	478	11.5
1987	118	89.5	21.2	34.3	7.1	74.0	288.0	.	7 17	332	693	13.0
1987	134	113.1	23.7	30.9	8.9	76.6	342.3	.	7.23	301	845	13.0
1987	195	17.7	13.3	28.4	3.4	82.3	55.0	.	7.54	.	347	7.0
1987	334	34.0	13.0	32.1	7.4	56.0	136.2	.	7.05	.	443	15.8
1987	336	5.8	5.7	14.4	4.1	26.0	33.1	.	7.16	.	162	13.0
1987	337	5.7	5.2	14.0	2.8	28.0	29.2	.	7.51	.	157	11.7
1988	85	144.4	29.4	30.9	4.6	74.2	455.4	.	7.19	.	1015	15.5
1988	206	20.4	13.5	40.1	2.2	83.0	73.0	.	7.00	.	399	7.0
SITE 5 (BACK CREEK)												
1983	312	26.2	14.0	16.9	1.1	34.0	103.0	7.4	6.88	341	264	17.0
1984	59	53.5	7.0	28.8	5.7	56.0	219.9	9.9	6.81	402	684	17.0
1984	135	68.4	35.9	30.7	2.9	64.0	296.4	5.0	7.54	435	800	11.0
1984	211	3.9	2.1	12.3	2.3	18.0	22.8	<0.5	7.27	363	.	9.9
1984	319	49.2	27.0	36.7	1.4	43.2	229.1	9.9	7.44	407	592	15.0
1986	233	68.0	40.0	27.4	1.4	64.7	308.6	9.1	7.59	435	800	11.0
1987	15	84.8	40.0	34.1	1.8	66.0	342.8	.	7.61	187	781	18.0
1987	55	90.4	43.1	39.6	6.5	87.0	328.1	.	7.31	370	984	16.0
1987	195	74.9	37.3	30.3	1.8	70.7	319.8	.	7.54	390	708	10.0
1988	87	95.8	40.5	37.4	1.0	70.1	359.9	.	7.86	.	895	16.0

YEAR	DAY	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Cl^{-}	ALK.	SO_4^{2-}	pH	Eh	COND	W_T
SITE 6 (TARA CREEK)												
1983	312	89.1	12.3	31.0	1.1	54.0	254.4	19.3	7.70	344	713	19.0
1984	59	84.4	12.5	37.6	3.5	61.0	237.5	16.5	7.32	351	720	18.0
1984	136	91.4	13.0	39.3	2.5	76.0	248.4	13.0	7.88	417	790	12.5
1984	319	79.4	11.5	45.0	2.8	65.4	262.2	15.6	7.60	407	696	18.0
1985	52	80.4	12.3	37.9	2.9	62.6	243.5	.	7.78	.	702	22.0
1985	127	80.0	12.2	39.2	3.1	61.2	229.0	.	7.63	.	709	14.0
1986	176	86.0	13.7	36.6	3.6	61.0	231.8	16.3	7.66	433	612	9.0
1986	233	77.7	13.0	37.3	2.1	63.7	226.2	15.1	7.82	431	616	12.5
1986	314	72.5	10.9	36.8	.	62.1	218.5	.	7.59	.	616	20.0
1987	15	72.1	12.3	39.2	2.6	60.0	213.7	.	7.32	401	624	19.0
1987	57	73.8	12.8	39.5	4.5	68.0	209.0	.	7.54	.	643	17.0
SITE 7 (SCRUBBY CREEK 4)												
1985	50	101.2	7.7	20.0	2.0	32.6	270.2	.	7.90	.	610	19.0
1985	128	93.0	6.3	18.5	1.8	34.0	242.7	4.8	8.11	418	589	15.0
1986	177	89.7	8.4	14.5	0.9	36.2	227.0	4.9	8.08	412	517	13.5
1986	232	85.2	8.0	16.0	1.1	36.4	225.6	4.0	8.02	425	539	14.0
1986	292	87.8	7.1	12.5	1.9	30.6	225.3	.	7.86	432	554	14.0
1986	314	88.8	7.6	14.3	.	35.9	232.1	.	7.80	.	595	14.0
1987	13	97.1	7.6	16.1	1.4	31.0	255.8	.	8.14	397	581	17.5
1987	55	91.3	8.1	16.9	1.4	32.0	248.2	.	7.98	427	600	17.0
1987	119	86.8	7.2	17.6	1.6	32.0	231.7	.	7.98	420	545	16.0
1987	134	83.8	7.8	16.5	1.9	34.2	224.8	.	7.82	391	510	16.0
1987	195	72.3	8.2	15.6	1.0	33.2	204.0	.	8.32	.	455	14.0
1988	85	87.0	7.9	16.4	1.3	31.5	225.0	.	8.08	.	552	17.0
1988	205	76.3	8.4	9.8	1.4	33.0	196.9	.	8.03	.	455	14.5
SITE 8 (NEW GUINEA 2)												
1982	296	24.4	8.1	15.2	2.2	21.0	90.0	8.6	7.80	411	275	13.5
1983	55	70.1	12.6	14.5	2.2	24.0	225.1	.	7.67	422	514	16.8
1983	313	26.2	4.8	8.1	1.7	19.0	81.7	2.4	7.37	386	240	14.0
1984	60	23.3	3.3	12.4	2.8	17.0	69.2	6.6	7.12	413	228	16.0
1984	137	29.2	4.8	11.1	3.0	19.0	93.3	2.0	7.09	448	260	13.0
1984	261	20.3	2.6	11.1	2.2	20.0	.	6.0	7.13	421	210	12.0
1984	320	20.2	3.5	15.0	7.5	18.2	78.5	3.9	7.39	409	232	14.0
1985	52	58.0	11.1	20.0	4.9	21.3	200.4	.	7.93	.	462	14.0
SITE 9 (NEW GUINEA 6)												
1982	296	27.3	5.5	11.8	1.6	16.0	86.7	7.8	8.00	414	245	14.0
1983	55	73.5	13.1	11.8	1.4	17.0	226.9	.	7.45	426	517	15.0
1983	313	44.8	5.3	7.9	1.6	20.0	119.8	2.9	7.43	426	310	13.0
1984	60	16.9	4.3	15.1	3.6	21.0	72.9	3.3	6.68	444	232	14.0
1984	137	26.8	6.6	15.5	4.3	22.0	95.1	2.0	7.19	439	290	13.0
1984	261	14.0	2.4	11.2	2.4	16.0	.	5.0	7.04	452	160	12.0
1984	320	14.1	3.7	23.5	3.8	18.6	.	3.0	7.52	420	198	13.0
1985	52	51.5	8.0	15.5	3.8	19.7	169.5	.	7.66	.	399	14.0

YEAR	DAY	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Cl^{-}	ALK.	SO_4^{2-}	pH	Eh	COND	W_T
SITE 10 (MOONS)												
1982	295	74.7	18.8	21.8	1.5	45.0	236.8	9.9	7.71	463	619	13.8
1983	54	90.7	15.7	21.0	3.1	43.0	264.7	.	7.49	438	610	16.0
1983	310	44.8	10.9	14.8	1.3	39.7	140.8	5.1	7.33	418	402	13.5
1984	59	24.9	8.5	22.2	4.4	43.0	92.8	3.3	6.87	409	301	16.0
1984	135	76.6	16.2	21.7	2.8	41.0	236.3	2.0	7.32	430	606	14.0
1984	210	11.9	2.9	14.4	2.2	21.0	48.1	<0.5	7.38	357	.	12.0
1984	259	34.1	7.3	16.3	1.9	27.0	104.9	11.0	7.43	430	306	13.0
1984	273	35.7	7.6	16.4	2.0	28.0	109.6	11.0	7.10	425	312	12.0
1984	318	45.6	11.0	19.0	2.5	34.3	154.8	11.6	7.24	.	442	13.5
1985	50	96.5	17.3	22.0	3.4	31.8	301.5	.	7.74	.	645	14.0
1985	126	64.9	11.4	23.3	3.5	44.4	187.8	.	7.54	.	567	15.0
1986	175	104.0	23.1	12.1	2.8	33.5	335.2	9.6	7.74	441	630	12.5
1986	231	74.8	21.8	28.3	2.8	85.5	200.9	9.9	7.75	440	658	14.0
1986	291	45.6	12.9	26.8	2.4	69.5	145.2	.	7.53	408	485	13.0
1986	315	78.9	14.6	19.4	.	50.5	226.1	.	7.41	.	659	13.0
1987	13	69.4	15.1	23.9	4.9	37.0	232.1	.	7.45	427	606	14.0
1987	54	73.8	12.8	39.5	4.5	68.0	209.0	.	7.37	413	600	14.0
1987	83	84.8	16.1	22.7	2.9	44.0	255.3	.	7.67	416	658	13.0
1987	118	88.8	15.9	23.0	2.7	42.0	277.2	.	7.49	424	640	14.0
1987	134	98.7	18.1	19.3	2.4	43.4	294.	.	7.34	.	668	14.0
1987	195	94.3	19.4	18.9	1.9	41.1	308.1	.	7.89	.	525	13.0
1987	334	84.6	14.8	21.8	1.5	41.0	243.9	.	7.38	.	566	13.9
1987	336	15.0	6.1	22.9	4.2	36.2	60.0	.	7.36	.	255	13.3
1987	336	13.8	5.6	17.5	3.5	33.0	54.6	.	7.31	.	208	13.3
1987	336	14.4	5.7	20.9	3.0	35.0	56.9	.	7.32	.	219	12.8
1987	337	20.0	7.1	21.8	2.5	30.0	80.0	.	7.51	.	260	12.8
1987	337	23.2	7.3	22.8	2.3	33.0	86.2	.	7.40	.	282	13.5
1988	85	96.8	16.3	20.1	2.8	38.2	280.3	.	7.96	.	610	14.2
1988	206	73.5	15.8	19.2	2.0	53.0	219.8	.	7.03	.	556	13.0
SITE 11 (M-4)												
1982	296	62.5	14.1	16.9	1.8	34.0	193.7	10.3	7.90	414	405	13.2
1983	311	95.2	12.1	11.4	1.6	33.0	258.0	11.1	7.32	391	504	15.0
1984	59	109.4	14.8	17.3	2.6	37.0	297.1	11.1	7.58	417	738	16.0
1984	137	96.4	15.0	17.3	2.8	38.0	270.9	8.6	8.21	411	756	15.0
1984	211	35.8	2.7	9.5	3.6	19.0	93.4	.	7.10	400	.	11.5
1984	260	54.3	6.0	14.1	3.1	26.0	142.8	5.0	7.13	430	389	15.0
1984	320	103.3	12.4	18.6	3.3	35.7	280.9	11.1	7.44	418	689	16.0
1985	52	107.0	14.1	18.7	3.4	39.4	303.5	11.5	7.74	.	708	17.0
1985	127	101.8	14.6	19.0	3.1	39.3	282.0	.	7.24	.	773	15.0
1986	176	110.6	16.1	15.2	2.2	39.0	297.1	8.6	8.01	425	882	15.2
1986	232	95.9	15.9	16.8	1.9	39.6	292.8	4.1	7.91	427	890	15.0
1986	292	102.0	15.0	14.8	2.8	34.4	286.8	.	7.53	429	668	15.0
1986	315	98.8	13.2	16.1	.	38.6	274.5	.	7.60	.	659	14.5
1987	13	109.8	14.5	18.0	2.7	37.0	299.0	.	8.01	404	690	15.0
1987	55	100.3	15.7	18.0	2.6	40.0	291.5	.	7.96	396	704	14.5
1987	138	97.6	13.4	15.3	2.4	39.1	276.5	.	7.61	.	592	14.0
1987	195	68.7	13.3	15.2	2.0	35.2	199.0	.	8.19	.	474	10.5
1987	334	99.0	13.1	18.3	1.6	35.0	290.1	.	7.69	.	723	15.5

YEAR	DAY	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Cl^{-}	ALK.	SO_4^{2-}	pH	Eh	COND	W_T
SITE 12a (SCRUBBY CREEK 1)												
1982	297	85.2	9.9	15.7	1.0	30.0	229.0	6.6	7.91	419	603	16.0
1983	55	89.0	8.7	16.2	1.3	35.0	234.9	.	7.68	413	600	17.0
1983	311	97.6	5.5	9.9	1.0	22.0	250.2	6.1	7.47	381	512	14.5
1984	61	124.5	8.0	17.8	1.5	31.0	320.6	11.9	7.45	398	732	17.0
1984	260	49.1	2.8	11.7	1.9	19.0	129.7	4.0	7.18	420	325	14.0
1984	272	64.1	3.6	12.9	1.9	21.0	169.5	5.0	7.12	423	407	14.0
1984	319	118.1	6.1	21.8	1.5	24.7	324.9	9.6	7.63	415	677	16.0
1985	51	125.0	7.8	20.1	2.3	35.0	334.0	.	7.76	.	714	16.0
1985	131	112.0	6.3	18.5	2.2	35.5	288.5	.	7.20	.	681	16.0
1986	177	107.7	8.5	15.2	0.9	37.0	265.2	4.9	7.51	401	570	16.5
1986	232	93.4	8.0	16.4	1.6	37.8	257.7	4.2	7.37	418	617	16.5
1987	13	121.3	7.7	16.0	0.5	31.1	310.	.	7.94	402	695	16.5
SITE 12b (SCRUBBY CREEK 2)												
1982	297	81.0	10.4	15.7	1.0	31.0	225.0	7.0	7.75	418	557	16.5
1983	55	96.8	10.0	16.2	1.2	36.0	250.4	.	7.66	422	600	17.0
1983	311	95.3	5.5	10.0	1.0	21.0	249.6	6.4	7.48	409	610	15.0
1984	61	124.5	8.0	17.8	1.5	33.0	318.4	13.2	7.06	406	677	16.0
1984	136	96.4	8.3	16.9	1.5	34.0	256.4	2.0	7.54	417	620	15.5
1984	210	27.0	1.1	8.3	3.0	9.0	80.0	<0.5	7.10	373	.	11.5
1984	259	48.7	3.0	11.6	2.2	18.0	127.9	4.0	7.05	427	330	14.0
1984	272	63.7	3.6	12.9	1.8	20.0	168.4	5.0	7.07	426	384	14.0
1984	319	103.7	6.0	19.8	1.5	24.4	292.1	9.6	7.63	.	677	16.0
1985	51	121.1	7.8	20.0	2.0	33.4	320.6	.	7.68	.	703	16.5
1985	128	109.6	6.3	18.5	2.0	35.4	280.0	.	7.74	.	671	16.0
1986	177	103.2	8.4	15.2	1.0	37.0	256.7	4.8	7.78	399	557	16.5
1986	232	91.9	8.5	16.6	.	38.1	254.7	.	7.74	.	572	16.0
1986	292	98.5	7.4	13.3	1.9	31.6	260.3	.	7.73	409	.	15.0
1986	314	101.0	7.7	14.5	.	35.5	263.4	.	7.56	411	649	15.0
1987	13	118.9	7.6	15.9	1.4	31.0	303.1	.	8.01	403	684	16.5
1987	55	119.4	8.5	17.0	1.4	32.0	311.4	.	7.83	421	713	16.0
1987	119	102.5	7.7	17.4	1.6	35.0	273.1	.	7.62	411	.	16.5
1987	134	97.0	7.7	16.0	1.9	34.2	266.5	.	7.62	403	593	16.5
1987	195	85.2	8.2	15.7	1.1	33.1	236.5	.	7.86	.	509	16.0
1988	85	109.5	8.5	16.7	1.3	31.7	282.2	.	7.62	.	629	16.5
1988	205	88.9	8.6	9.6	1.5	33.0	232.5	.	7.65	.	518	16.2

YEAR	DAY	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Cl^{-}	ALK.	SO_4^{2-}	pH	Eh	COND	W_T
SITE 12c (SCRUBBY CREEK 3)												
1982	297	69.1	10.3	15.8	1.0	31.0	196.5	10.3	8.15	406	513	18.0
1983	55	85.6	9.0	16.3	1.2	36.0	228.2	.	7.90	414	570	19.5
1983	311	89.8	5.5	9.9	1.0	22.0	249.7	8.3	7.96	405	528	16.5
1984	61	111.1	8.1	17.6	1.5	32.0	285.4	5.8	7.51	424	576	16.0
1984	135	86.5	8.4	17.6	3.2	34.0	231.5	2.0	7.87	415	493	14.5
1984	210	27.0	1.1	8.3	3.0	9.0	80.0	<0.5	7.10	373	.	11.5
1984	260	49.1	2.9	11.5	2.2	18.0	132.0	4.4	7.21	427	319	14.0
1984	272	63.3	3.6	12.7	1.7	21.0	167.2	4.6	7.12	423	390	14.0
1984	319	99.0	6.1	19.8	1.5	24.0	273.6	9.6	7.76	418	627	16.0
1985	51	104.2	7.8	20.0	2.0	33.0	277.7	.	7.98	.	633	19.0
1985	128	96.3	6.3	18.5	2.0	34.5	250.0	.	8.04	.	603	16.0
1986	177	92.0	8.5	15.2	1.0	36.4	229.4	4.8	8.16	427	523	15.0
1986	232	89.4	8.0	16.0	1.6	36.8	229.9	4.0	8.12	386	541	15.0
1986	314	95.0	7.6	14.3	.	35.9	233.8	.	7.60	.	589	15.0
1987	13	101.2	7.4	16.2	1.4	31.0	261.7	.	8.23	407	593	17.0
1987	55	.	.	.	.	.	254.9	.	8.01	.	617	16.5
1987	119	86.3	7.6	18.1	1.6	29.0	232.5	.	7.82	418	545	16.5
1987	134	82.6	7.9	16.3	2.1	34.5	225.7	.	7.80	406	515	16.5
1987	195	73.1	8.0	15.7	1.1	33.1	204.9	.	8.14	.	461	15.0
1988	85	89.9	8.2	16.7	1.3	31.8	232.0	.	7.94	.	560	17.0
1988	205	71.9	8.0	9.6	1.5	33.0	190.6	.	7.96	.	450	15.2
SITE 13 (BITCH OF A DITCH)												
1982	296	122.4	39.3	31.5	1.2	65.0	416.7	12.1	7.00	418	1003	18.0
1983	55	126.7	38.3	33.0	1.2	68.0	424.2	.	7.19	412	.	17.2
1983	311	115.2	32.7	19.4	0.8	49.0	392.7	13.6	7.35	414	1056	17.0
1984	59	123.6	37.4	30.0	1.6	62.0	413.2	9.9	7.96	415	960	17.0
1984	136	124.4	37.1	28.8	1.7	65.0	414.6	2.0	7.12	423	968	16.5
1984	211	103.5	16.5	13.8	0.8	17.0	333.4	2.1	7.11	375	.	16.0
1984	259	99.6	22.6	18.5	0.8	36.0	330.4	2.1	7.27	445	710	17.0
1984	318	110.6	30.3	39.3	1.7	53.2	394.4	12.7	7.17	426	871	16.5
1985	50	122.0	37.8	28.8	2.0	60.1	415.6	.	7.47	.	972	17.0
1985	128	124.0	32.7	29.9	1.9	63.8	412.2	.	7.49	.	1056	17.0
1986	175	124.1	39.8	26.5	1.4	61.4	407.7	11.9	7.42	433	1080	17.0
1986	233	109.1	39.5	27.4	1.0	61.5	413.8	12.0	7.49	425	956	16.5
1986	314	126.7	35.7	26.6	0.8	62.2	412.9	.	7.48	384	954	17.0
1987	13	124.3	36.9	28.6	1.6	59.0	413.2	.	7.86	404	968	16.5
1987	55	120.3	39.6	29.1	1.6	61.0	420.5	.	7.61	418	.	17.0
1987	83	118.8	41.4	28.9	1.5	58.0	418.7	.	7.58	413	959	17.0
1987	119	119.5	38.6	30.7	1.7	63.0	426.2	.	7.51	405	928	17.2
1987	135	119.2	36.1	28.8	2.6	63.6	422.2	.	7.50	406	937	16.5
1987	195	116.4	34.6	25.2	1.2	58.9	418.0	.	7.44	.	859	17.0
1988	85	122.3	37.0	30.2	1.5	59.5	413.4	.	7.81	.	952	17.5

YEAR	DAY	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Cl^{-}	ALK.	SO_4^{2-}	pH	Eh	COND	W_T
SITE 14 (DUKES)												
1982	295	163.8	34.3	90.0	2.7	220.0	366.5	24.3	6.93	437	1500	17.0
1983	54	178.3	36.2	83.9	3.9	256.0	390.5	.	6.78	483	1616	18.0
1983	207	104.9	18.3	46.9	2.2	137.2	265.6	9.0	.	.	900	16.0
1983	310	100.7	17.9	35.1	1.6	99.0	255.2	13.3	7.05	414	861	16.0
1984	59	163.7	31.6	71.9	3.4	212.0	370.1	16.9	6.62	422	1380	17.0
1984	135	163.9	33.9	80.8	5.2	240.0	380.4	11.0	6.84	418	1440	17.0
1984	210	60.5	11.8	41.2	4.1	68.3	194.0	4.2	7.43	380	.	13.0
1984	259	64.5	10.9	29.1	2.4	61.0	165.4	9.4	7.18	427	540	16.0
1984	273	66.1	10.8	28.7	2.3	60.0	171.1	10.0	7.24	425	540	15.0
1984	318	120.7	20.9	60.6	3.5	134.9	315.8	21.5	7.27	405	1095	17.0
1985	50	160.0	28.9	70.5	3.9	203.9	366.0	16.0	7.17	.	1355	16.5
1985	126	165.9	30.1	78.3	3.9	203.9	366.0	15.0	7.10	.	1440	17.0
1986	175	161.8	34.0	74.8	2.7	206.8	366.1	16.9	7.13	413	1296	17.0
1986	231	157.8	35.0	71.3	2.1	217.1	373.9	16.9	7.30	437	1377	16.0
1986	291	156.8	31.3	74.3	2.9	209.5	368.7	.	7.12	394	1439	16.5
1986	315	164.4	31.4	74.9	.	224.4	359.3	.	7.21	.	1430	16.5
1987	13	158.9	30.5	69.8	3.2	194.0	361.1	.	7.45	412	1365	16.0
1987	54	165.2	35.8	77.7	3.7	223.0	383.1	.	7.27	401	1476	16.5
1987	56	164.7	35.8	77.4	3.7	225.0	377.2	.	7.27	395	1452	16.5
1987	83	153.4	33.8	69.4	3.0	205.0	364.9	.	7.23	419	1331	16.5
1987	118	162.0	35.5	76.8	4.1	226.0	381.5	.	7.31	393	1440	17.0
1987	134	165.0	34.2	80.6	3.7	241.5	387.2	.	7.12	420	1458	17.0
1987	195	163.5	34.0	80.6	3.1	252.2	394.7	.	7.06	.	1452	17.0
1987	334	144.3	29.4	77.6	2.6	206.0	352.4	.	6.89	.	1344	17.2
1987	336	145.9	29.4	78.9	2.7	211.0	359.4	.	6.84	.	1362	17.2
1987	336	146.3	29.4	77.6	2.7	212.0	355.5	.	6.86	.	1328	17.0
1987	336	145.9	29.6	79.3	2.7	211.0	359.4	.	6.96	.	1350	16.9
1987	337	144.3	29.6	78.9	2.7	210.0	354.0	.	6.96	.	1344	16.7
1987	337	143.9	29.4	79.3	2.7	210.0	354.0	.	6.98	.	1331	16.9
1988	85	171.8	35.1	83.8	3.0	236.5	397.0	.	7.12	.	1510	18.0
1988	206	155.1	30.5	77.0	3.1	233.0	353.2	.	7.02	.	1341	17.5
SITE 15 (SCROOGES VAULT)												
1985	130	108.6	12.9	31.9	3.1	99.3	221.0	.	7.18	407	840	17.0
1986	291	128.1	25.5	66.3	3.4	203.0	244.6	.	7.31	405	1159	15.0
1986	312	120.5	22.4	63.0	.	200.0	224.4	.	7.31	441	1112	16.5
1987	14	124.8	21.2	55.7	2.7	179.0	235.6	.	7.51	412	1035	16.5
1987	83	111.3	23.1	57.0	2.9	174.0	279.7	.	7.24	423	1107	16.5
1987	120	107.8	24.1	57.8	3.2	180.5	220.9	.	7.11	400	984	17.0
1988	86	126.2	22.9	61.1	2.2	192.2	237.6	.	7.50	.	1064	17.0

YEAR	DAY	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Cl^{-}	ALK.	SO_4^{2-}	pH	Eh	COND	W_T
SITE 16 (B-67)												
1982	297	187.0	43.2	102.5	2.9	306.0	405.9	33.3	6.85	412	1824	17.0
1983	55	188.6	39.9	110.0	2.9	305.0	408.8	.	7.09	369	1771	19.0
1983	311	174.5	39.8	89.9	2.0	297.0	398.3	24.7	6.77	354	1722	16.0
1984	61	187.1	42.0	106.1	3.9	308.0	411.0	23.9	7.06	368	1630	16.0
1984	137	180.4	40.4	106.5	3.5	312.0	404.9	14.1	6.98	418	1720	16.0
1984	210	42.2	6.8	23.7	1.9	41.0	116.9	3.1	7.14	337	.	12.0
1984	272	114.8	25.9	67.6	2.9	188.0	262.6	13.0	7.13	425	1122	16.0
1984	319	180.1	37.6	98.0	5.0	304.9	409.3	24.0	7.05	427	1722	16.0
1985	50	187.5	38.6	105.0	3.9	304.1	402.0	.	7.12	.	1758	17.0
1985	130	186.9	40.1	109.4	4.3	308.9	405.3	.	6.90	.	1800	17.0
1986	176	182.4	43.0	109.3	3.1	296.3	401.1	14.4	6.86	420	1754	17.0
1986	233	174.7	43.4	104.4	3.1	299.0	404.1	31.0	7.17	429	1620	17.0
1986	291	177.8	38.5	106.5	3.1	303.9	406.1	.	7.31	387	1701	17.0
1986	312	177.3	38.4	106.0	.	298.9	400.2	.	7.14	.	1693	17.5
1987	14	186.2	39.9	103.6	4.0	288.0	402.6	.	7.39	414	1691	16.5
1987	83	174.7	44.2	102.1	3.8	294.0	408.8	.	7.03	430	1647	16.5
1987	118	174.6	41.6	102.3	4.3	291.0	408.8	.	7.10	421	1638	17.0
1987	135	175.6	38.6	99.3	3.7	301.3	407.2	.	7.09	408	1654	16.5
1987	196	171.8	38.3	97.8	3.1	307.0	411.4	.	6.99	.	1500	17.0
1987	336	165.1	37.9	104.2	3.0	295.0	391.7	.	6.94	.	1638	16.4
1988	86	181.7	40.3	104.1	3.0	290.3	398.0	.	6.98	.	1710	17.0
1988	205	176.4	38.5	111.1	3.0	313.0	401.4	.	7.01	.	1633	17.0
SITE 17 (B-41)												
1985	130	188.9	40.2	108.2	4.5	308.9	406.5	26.8	6.97	418	1809	16.5
1986	176	186.2	43.3	108.9	3.0	300.0	402.9	14.1	6.90	411	1599	16.0
1986	233	159.1	42.9	104.0	2.7	300.0	408.9	21.0	7.05	428	1540	16.0
1986	312	182.9	39.3	106.0	.	297.8	396.6	.	7.20	.	1667	17.5
1987	14	187.5	40.3	103.2	3.8	288.0	402.6	.	7.21	414	1672	16.5
1987	55	160.9	41.4	95.6	4.0	275.0	378.1	.	7.09	430	1573	16.5
1987	83	178.2	43.9	99.5	3.8	292.0	408.8	.	7.09	439	1657	16.5
1987	118	171.0	38.5	96.4	4.0	286.0	407.1	.	7.09	406	1602	17.0
1987	135	175.6	38.6	99.8	4.6	301.9	408.9	.	7.12	401	1624	16.5
1987	196	172.6	38.3	99.5	3.2	307.4	409.7	.	7.11	.	1525	15.0
1987	336	144.8	34.3	78.5	2.3	225.0	337.0	.	6.96	.	1281	14.7
1988	86	180.2	40.3	103.3	3.1	289.6	386.2	.	6.89	.	1691	16.8
1988	205	176.4	37.9	112.0	3.0	314.0	401.5	.	6.97	.	1601	16.5
SITE 18 (UN-NAMED SEEP)												
1983	313	70.5	22.8	18.8	2.1	39.0	232.8	23.5	6.70	385	720	12.0
1984	60	101.9	26.6	18.7	2.6	30.0	333.9	15.2	7.12	412	805	19.0
1984	137	121.1	28.2	18.9	1.4	33.0	385.7	15.0	7.05	431	1001	9.5
1984	261	31.8	9.2	5.7	2.0	26.9	101.7	9.0	7.11	410	302	14.5
1984	320	102.8	25.2	26.5	3.2	27.2	363.5	21.1	7.13	406	805	19.0

YEAR	DAY	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Cl^{-}	ALK.	SO_4^{2-}	pH	Eh	COND	W_T
SITE 19 (UN-NAMED CREEK)												
1984	211	18.3	0.8	3.8	3.4	7.3	55.5	.	7.15	414	.	11.0
1984	260	79.9	4.5	9.7	1.1	12.0	215.2	5.6	8.05	409	455	19.0
1984	272	94.1	4.8	10.2	1.0	14.0	249.7	6.0	7.34	423	499	14.0
1984	319	79.3	4.8	16.3	0.9	13.5	230.0	6.8	7.93	403	483	19.0
SITE 20 (BUTCHERS CREEK)												
1987	119	8.1	5.4	13.5	2.8	28.5	31.4	.	7.24	428	167	13.5
1987	134	7.0	5.0	13.5	2.9	28.1	30.8	.	7.10	414	161	14.0
1987	195	14.5	10.5	17.0	2.2	50.3	51.6	.	8.12	.	270	7.0
1987	334	9.6	7.0	15.3	2.8	31.0	43.9	.	7.36	.	193	21.0
SITE 21 (SUB-AQUA)												
1983	313	27.9	6.7	9.2	1.4	21.0	87.7	4.9	7.35	405	258	16.0
1984	59	29.6	8.1	14.6	3.0	26.0	99.0	6.2	7.34	409	291	20.0
1984	137	20.2	7.9	14.5	2.6	34.0	69.1	2.0	7.08	421	262	11.0
1985	52	40.9	9.3	18.4	4.8	28.6	143.5	4.9	7.86	.	380	19.0
1985	127	29.7	8.7	17.1	3.9	35.4	98.5	4.3	7.68	.	325	14.0
SITE 22a (SPRING CREEK FALLS)												
1987	118	20.7	14.5	35.4	5.9	81.0	77.8	.	7.31	425	435	11.5
1987	134	21.1	16.5	29.9	5.4	68.4	101.0	.	7.39	398	460	13.0
1987	334	17.2	14.5	33.9	3.9	60.0	90.8	.	6.89	.	289	15.3
SITE 22b (SPRING CREEK UPSTREAM SITE 14)												
1987	334	121.6	25.7	57.5	2.3	146.0	315.5	.	7.16	.	1027	15.8
SITE 22c (SPRING CREEK BETWEEN SITES 14 AND 10)												
1985	50	148.6	26.8	68.9	3.9	195.7	354.0	.	7.91	.	1230	16.0
1987	334	143.5	28.4	78.0	2.6	208.0	352.4	.	7.54	.	1224	16.7
1987	336	24.1	8.9	28.6	3.8	49.0	87.0	.	7.54	.	301	13.9
1988	85	168.4	34.3	84.6	2.9	235.6	376.8	.	7.61	.	1487	18.0
SITE 23 (FEDERAL CAVE)												
1984	210	79.9	3.4	9.7	1.3	11.0	222.4	4.1	7.10	.	.	10.5
1988	85	59.5	3.6	7.1	0.8	15.7	155.4	.	7.55	.	354	16.8

YEAR	DAY	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Cl^{-}	ALK.	SO_4^{2-}	pH	Eh	COND	W_T
SITE 24 (FAIRY CREEK)												
1984	210	5.9	3.4	9.9	3.4	16.3	29.2	.	7.40	407	.	11.0
1984	259	15.6	5.2	18.9	2.7	22.0	52.9	14.0	7.63	437	212	13.0
SITE 25 (WILSONS CAVE)												
1984	210	6.7	2.5	10.0	3.7	15.0	30.0	.	7.60	.	.	11.5
SITE 26 (ROYAL CAVE)												
1984	259	66.9	3.6	11.8	1.2	18.0	172.4	8.0	7.88	428	390	16.0
SITE 27 (SCRUBBY CREEK ABOVE)												
1987	55	20.1	5.4	17.1	4.9	21.0	78.3	.	7.61	421	241	15.0
SITE 28 (FARM DAMS)												
1983	54	4.1	6.7	23.2	12.7	38.0	43.9	.	7.96	317	247	23.0
1988	86	2.4	11.1	29.8	12.2	52.9	52.6	.	7.96	.	283	28.0
SITE 29 (UN-NUMBERED BOREHOLE)												
1987	14	1.7	1.7	17.0	7.0	14.0	33.7	.	7.93	380	149	16.5
SITE 30 (TEA-TREE CREEK)												
1988	207	14.0	4.8	16.4	1.3	35.0	38.1	.	7.02	.	197	8.0
SITE 31 (OVERLAND FLOW)												
1984	210	23.0	0.5	13.8	5.4	12.0	87.5	.	7.10	.	.	11.0
SITE 32 (BELOW BITCH OF A DITCH)												
1987	135	110.3	36.4	28.8	2.6	63.6	398.1	.	7.68	413	924	17.0
1987	119	111.0	38.4	30.8	1.8	62.0	402.2	.	7.81	398	845	19.0
SITE 33 (RAINFALL)												
1983	311	0.72	0.11	0.53	0.49	0.73	.	.	.	.	.	.
1984	210	0.40	0.05	0.21	0.04	0.56	.	.	5.48	.	.	9.0
1985	130	0.83	0.12	0.47	0.53	.	.	.	.	.	.	.

APPENDIX B.

SAMPLE SITE NUMBERS AND SITE NAMES.

SITE NUMBER	SITE NAME
1)	Buchan River
2)	Murrindal River
3)	Snowy River
4)	Spring Creek
5)	Back Creek
6)	Tara Creek
7)	Scrubby Creek 4
8)	New Guinea 2
9)	New Guinea 6
10)	Moons
11)	M-4
12a)	Scrubby Creek 1
12b)	Scrubby Creek 2
12c)	Scrubby Creek 3
13)	Bitch of a Ditch
14)	Dukes
15)	Scrooges Vault
16)	B-67
17)	B-41
18)	Un-named Seep
19)	Un-named Creek
20)	Butchers Creek
21)	Sub-Aqua
22a)	Spring Creek (Falls)
22b)	Spring Creek (upstream site 14)
22c)	Spring Creek (between sites 14 and 10)
23)	Federal Cave
24)	Fairy Creek
25)	Wilsons Cave
26)	Royal Cave
27)	Scrubby Creek (above)
28i)	Farm dam
28ii)	Farm dam
29)	Un-numbered borehole
30)	Tea-Tree Creek
31)	Overland flow
32)	Bitch of a Ditch (below)
33)	Rainwater