THE EQUILIBRIUM HYDROGEOCHEMISTRY OF DAVYS CREEK, CENTRAL NSW.

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ABSTRACT

Davys Creek (32°40' S, 148°40' E) is a tributary of the Belubula River in central western N.S.W. Springs that source Davys Creek are enriched in dissolved calcite (as Ca^{2+} and HCO_3^-), resulting in one of the few calcite-precipitating streams in NSW. Coupled with atmospheric CO_2 degassing, calcite precipitation has been shown to occur in regions of stream turbulence, where CO_2 exsolution is at a maximum. Temperature influences the solubility of both Ca^{2+} and HCO_3^-, and with samples taken over 16 months, this study allowed for seasonal interpretation. Results are consistent with previous research and present a valuable insight into the equilibrium hydrogeochemistry of Davys Creek.

BACKGROUND

The equilibrium chemistry of the $CO_2/H_2O/CaCO_3$ system is the dominant influence on karst systems (White, 1988; Gillieson, 1996), for it controls the dissolution and precipitation of rocks and minerals by natural waters and consequently the geomorphology of karst environments (Jennings, 1985; Ford, 1992). Table 1 introduces dominant equilibria reactions that occur along hydrological pathways within karst environments.

Table 1: Simplified processes of solution of calcium carbonate (Gillieson, 1996).

EQUATION	KINETICS	
$CO_{2(g)} + H_2O \rightleftarrows CO_{2(aq)} + H_2O$	(slow)	(1.1)
$CO_{2(aq)} + H_2O \rightleftarrows H_2CO_3$	(slow)	(1.2)
$H_2CO_3 \rightleftarrows H^+ + HCO_3^-$	(fast)	(1.3)
$H^+ + CO_3^{2-} \rightleftarrows HCO_3^-$	(fast)	(1.4)
$CaCO_3 \leftrightarrows Ca^{2+} + CO_3^{2-}$	(slow)	(1.5)

Exposed limestone (as calcite ($CaCO_3$) rocks) occurs on about 20% of the Earth's surface (Langmuir, 1997). If mineral carbonates of calcium and magnesium are present at levels of >1%, they will tend to dominate the chemistry of the soil and groundwater (Langmuir, 1997). Dissolved limestone contributes calcium ions by the overall dissolution equation (Stumm and Morgan, 1996; Dreybrodt, 1998):

$$CaCO_3 + CO_2 + H_2O \rightleftarrows Ca^{2+} + 2HCO_3^- \qquad (1.6)$$

The relative calcium ion (Ca^{2+}) concentration increases with respect to dissolved CO_2 (as HCO_3^-), and as the solution becomes supersaturated, the reverse reaction of equation (1.6) may occur. The degree of saturation is usually determined with reference to the calcite saturation index:

$$SI_c = \log (IAP_c/K_c) \qquad (1.7)$$

where IAP_c is the ion activity product ($\alpha Ca^{2+}. \alpha CO_3^{2-}$) for a given water sample and K_c is the solubility product constant for calcite (Stumm and Morgan, 1996; Langmuir, 1997). For a supersaturated water, $SI_c > 0$, and for an under-saturated solution $SI_c < 0$. The further from 0, positive or negative, infers the degree of supersaturation or under-saturation respectively.

Spring water emerging at the Earth's surface will release carbon dioxide to attain atmospheric equilibrium through degassing, driving the SI_c upward (Ford, 1989; 1992). Degassing of CO_2 is enhanced by stream turbulence (Herman and Lorah, 1987; Liu *et al*, 1995) and an increase in water temperature (Drake, 1983; Dreybrodt *et al.*, 1996). Aquatic vegetation also uses CO_2 during photosynthetic respiration (Ford, 1989; Ford & Pedley, 1996).

Spring water can be differentiated from surface water by hydrochemical analysis, i.e. a relatively lower pH, higher Ca^{2+} and HCO_3^- concentrations, a higher SC and a lower calcite saturation index (SI_c). These parameters vary as carbonate spring water flows downstream and gains atmospheric equilibrium, with respect to CO_2, and may result in calcite precipitation (Herman and Lorah, 1987; Liu *et al*, 1995; Drysdale *et al*, 1998).

Calcium carbonate is preferentially precipitated due to the lower solubilities of other ions in solution (Katz, 1973; Dreybrodt, 1988). For calcite to precipitate, a suitable nucleation site must be available (Dreybrodt, 1988). In solution, the presence of excess cations with larger ionic radii (ie, Mg^{2+}) can inhibit calcite precipitation by decreasing the availability of suitable nucleation sites (Morse, 1983).

Calcite precipitation does not usually occur at the source of non-thermal springs due to the slow rate of CO_2 ex-solution. The degree of calcite saturation, governed on the surface by degassing, temperature and stream geomorphology, influence downstream CO_2 loss and control where calcite, if any, is deposited. Temperature affects the solubility of CO_2 and Ca^{2+} in solution and has been found to have an important influence on the equilibrium chemistry of carbonate ground waters (Drake, 1983) and spring waters (Liu *et al*, 1995).

SITE DESCRIPTION

Davys Creek exists on two private properties, namely "Boonderoo" and "North Werribee", approximately 30 km north east of Cowra and 50 km west south west of Orange. The Davys Creek catchment is comprised predominantly of andesite and limestone. The andesite (Walli Andesite) occupies around two-thirds of the upper surface catchment and has uplifted during the early to mid Ordovician (Webby and Packham, 1982).

The limestone unit (Cliefden Caves Limestone Group) occupies the lower third of the surface catchment and formed in the mid to late Ordovician (Webby and Packham, 1982). Consisting of seven sub-groups, the Cliefden Caves Limestone Group will be herein referred to as the "limestone" (Figure 1).

The limestone is heavily folded, with several fault lines transecting Davys Creek in a north west-south east direction. The exposed bedding planes of the limestone can be seen in places, particularly near contacts with the Walli Andesite. Block faulting has resulted in the older Walli Andesite being above the younger limestone (Hill, 1999).

The elevation of the Davys Creek catchment ranges from approximately 585 metres on the Walli Andesite, to around 400 metres at its confluence with the Belubula River. The Walli Andesite/ limestone contact can be seen to strike (NE-SW) across Davys Creek 3 km downstream from the head of the catchment, at an elevation of approximately 450 m.

A further 1 km downstream at an elevation of 430 metres, a small outcrop of exposed Walli Andesite exists within Davys Creek. Between the limestone, the exposed Walli Andesite outcrop covers a downstream distance of 150 metres, coinciding with the Wonga fault line (Figure 1). Limestone is present for the last 900 metres of Davys Creek.

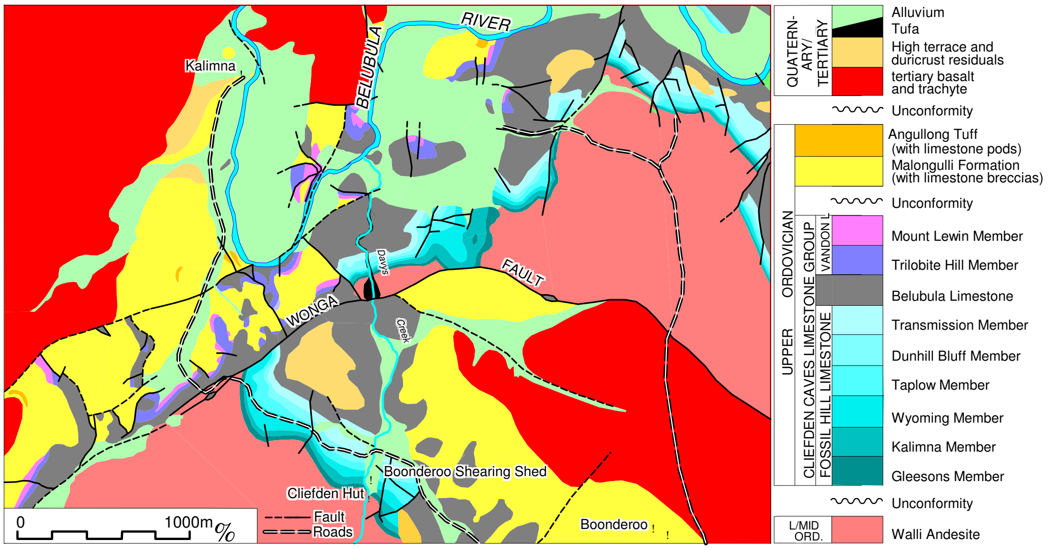


Figure 1: Surface Geology of Davys Creek (Adapted from Webby and Packham, 1982)

HYDROLOGY & GEOMORPHOLOGY

Davys Creek commences on the Walli andesite to the south of the limestone. The first 600 metres of Davys Creek, on “North Werribee”, is dominated by two farm dams. No flow was observed between here and a conspicuous reed bed a further 500 metres downstream, ultimately becoming Site 1 (S1), the point chosen to begin this study.

The gradient is relatively low (Figure 2) from S1 to S4 where a further two farm dams exist. Downstream of the second farm dam, Davys Creek has incised through the thick alluvium forming terraces. Cattle use Davys Creek for drinking purposes and cause severe bank erosion in some areas on the Walli Andesite.

The gradient was relatively low along this reach, and sediment deposition was evident over the next 1 km. The sediment favoured deposition around willow trees, where the semi-exposed root systems captured larger debris during storm events, eventually forming the sediment dams observed.

Approximately 400 metres prior to the Walli Andesite/limestone contact, the gradient steepens through a rocky reach of Davys Creek. Calcite precipitation can be observed, in the form of tufa barrages, which contain encrusted sticks and tree branches. This continues to a weir, approximately 5 metres upstream of the Walli Andesite/limestone contact, where the largest tufa deposit on the Walli Andesite exists (~1 metre).

Downstream of the Walli Andesite/limestone contact, Davys Creek flows for another 300 metres before sinking into the limestone. The dry channel meanders through more alluvial terraces, much larger than the terraces observed on the Walli Andesite, for another 450 metres. Spring water emerges near the downstream Walli Andesite/limestone contact. Flowing onto the Walli Andesite outcrop, spring waters deposit tufa approximately 100 metres from the spring source. Fossil tufa deposits can be observed on the adjacent alluvial terraces of Davys Creek, inferring a higher stream position than the present day.

The gradient increases sharply over the next 500 metres through heavily folded limestone. Dominated by active tufa deposition, this reach displayed small tufa barrage systems and dams (~3 metres), forming a series of cascades and waterfalls. The gradient decreases substantially in the lower reaches, where flow continues until its confluence with the Belubula River a further 150 metres downstream.

METHODS

A monitoring schedule was implemented that involved up to 20 water sample sites, dependent on flow (Table 2). Sample sites were selected above, through, and below observed calcite precipitation sites, and also included spring sources, a sink, and an anthropogenic dam (Figure 2). Although numerous site visits were made, the four most extensive campaigns will be presented. The specific dates for the monitoring schedule are outlined below:

Table 2: Davys Creek field trips

DATE	NUMBER OF SAMPLES TAKEN
MAR99 - 13/3/1999	19
JULY99 - 24/7/1999	19
OCT99 -3/10/1999	20
FEB00 - 12/2/2000	19

Analysis was performed using a calibrated Eutech CyberScan PC10 hand held pH/Conductivity/Temperature Meter. Sample bottles were rinsed three times in creek water at the sample site before sampling. The sample bottle was then filled to capacity to minimise gas exchange, and reduce errors in the bicarbonate analyses (alkalinity) (APHA, 1998). The sample was filtered through a 0.45µm membrane filter, using a Millipore hand vacuum pump, to remove suspended solids.

After taking the required aliquot for bicarbonate (HCO_3^-) analysis, which was analysed on site, the sample was mixed thoroughly and divided into two 100 ml sub-samples. One 100 ml bottle (cations) was acidified with 2 ml of concentrated nitric acid (HNO_3), and the other left non-acidified for anion analysis. Both were refrigerated below 4^oC and analysed within 7 days (APHA. 1998).

Cation analysis was performed using an ARL 3520 ICP-AES. Major cations analysed for were calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), and potassium (K^+). The major anions measured for were bicarbonate (HCO_3^-), chlorides (Cl^-), sulfates (SO_4^{2-}), and nitrates (NO_3^-). Bicarbonate (HCO_3^-) concentration was achieved by the potentiometric titration method against a dilute HCl solution, within 24 hours of sampling. Chlorides (Cl^-), nitrates (NO_3^-) and sulfates (SO_4^{2-}) were measured using a Waters^{TM} Ion Chromatograph (IC), using the IC method (APHA, 1998). Only results pertaining to changes in the $CO_2/H_2O/CaCO_3$ equilibrium system are presented during discussion.

RESULTS & DISCUSSION

Researchers have shown that regions of hydrochemical variability in carbonate water systems directly relate to regions of stream turbulence (Lorah & Herman, 1988; Lui & Dreybrodt, 1997; Drysdale & Gale, 1997). These regions were also deemed to be the most effective sites to measure the downstream evolution in the hydrogeochemistry of Davys Creek. Three segments of downstream hydrogeochemical evolution were identified, and for ease of discussion, will be interpreted separately.

Downstream variation in Ca^{2+} and HCO_3^- concentrations

Sites S1-S4

Spring water emerging at the uppermost spring in the Davys Creek catchment is saturated with dissolved CO_2 (as HCO_3^-) and Ca^{2+}. As spring water flows downstream, CO_2 degasses from solution to attain atmospheric equilibrium, and is reflected in the decreasing HCO_3^-. In studies at Falling Spring Creek, Virginia USA, Herman and Lorah (1988) have shown that CO_2 is lost from solution immediately as water emerges from a carbonate spring, due to its tendency to equilibrate with the atmospheric CO2 gradient. Precipitation of calcite from a calcite-saturated solution will not happen immediately as supersaturation is reached and subsequently no calcite precipitation was observed in the immediate downstream vicinity of S1.

The increased residence time in pooled surface waters favoured evaporation and natural degassing, which appeared to be the main influences on decreasing HCO_3^- concentrations between S1 and S4. The ephemeral nature between S2 and S3 meant that discharge variation in surface flow at any one site was relatively large, from no surface flow to maximum flow during storm events. The first farm dam, prior to S2, acts as a surface storage for spring water from S1. Just as increased residence time underground increases the dissolved CO_2 concentration, increased residence time on the surface will allow the exposed water to atmospherically degass over time, until equilibrium is reached. Rainfall will also have a dilution effect during prolonged rain events.

Figure 2: Sample Sites and Long Profile of Davys Creek, central NSW.

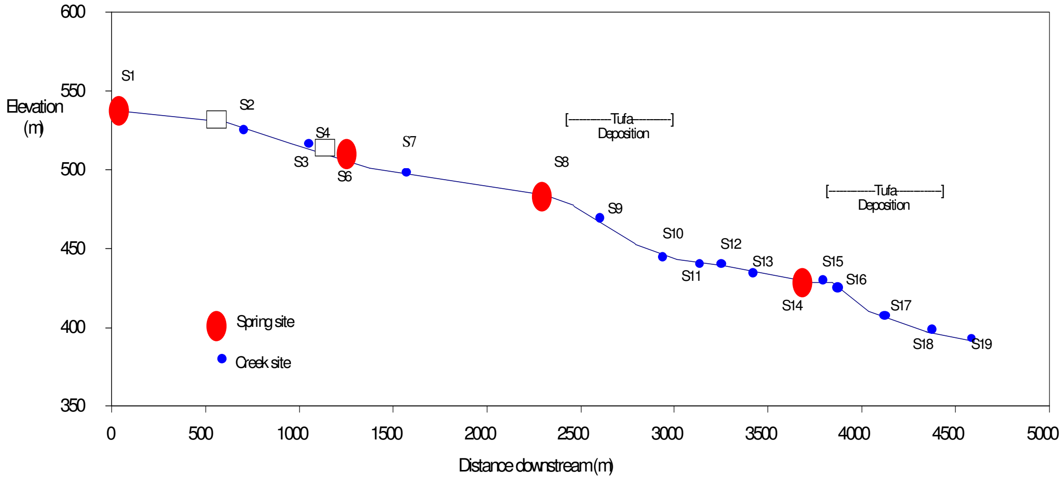


Figure 3: Downstream Variation in $[Ca^{2+}]$ Davys Creek, central NSW.

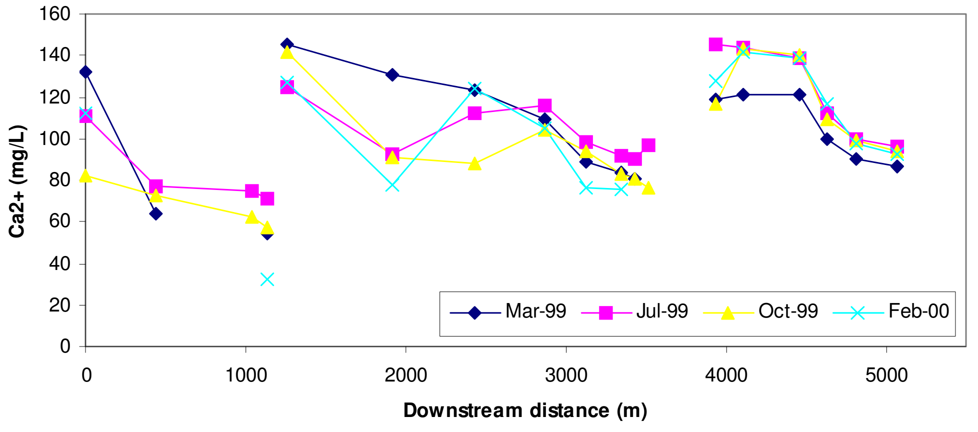


Figure 4: Downstream Variation in [HCO_3^-]
Davys Creek, central NSW.

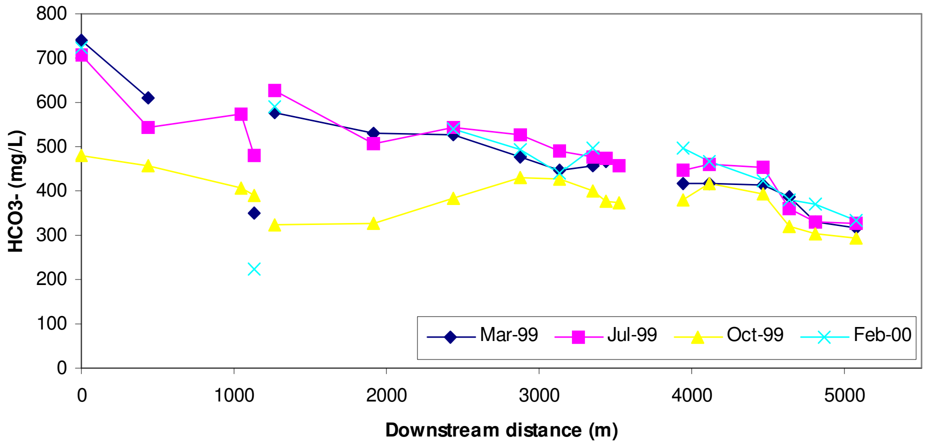


Figure 5: Downstream Variation in SI_c
Davys Creek, central NSW.

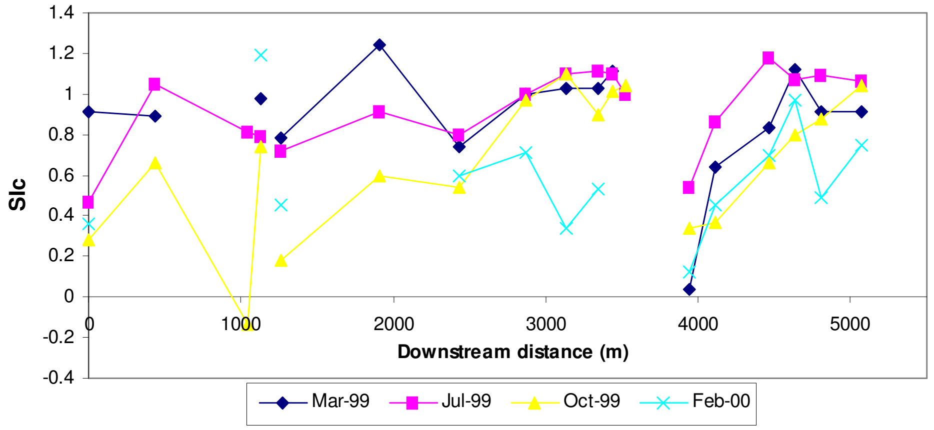
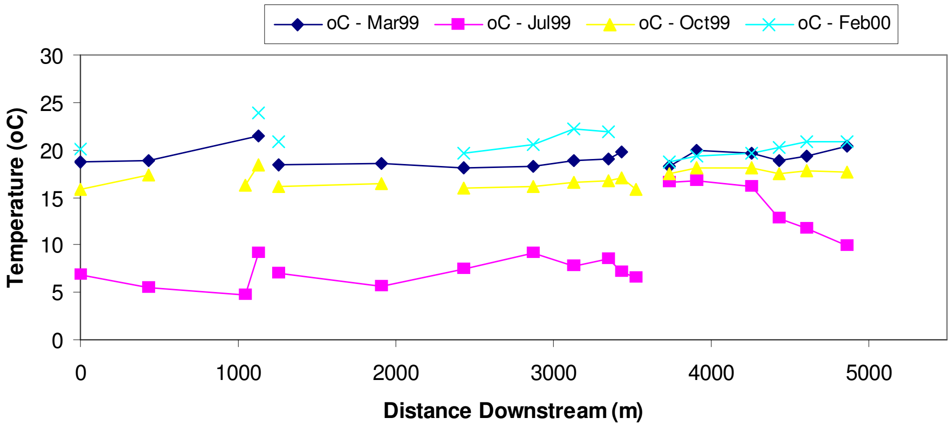


Figure 6: Downstream Variation in Temperature (°C)
Davys Creek, central NSW.



Hydrogeochemical data also confirms that Ca^{2+} is lost from solution between S1 and S4 (Figure 3). Suarez (1983) studied the downstream variation in calcite saturation in the Colorado River, and noted that decreasing levels of Ca^{2+} can be measured without any observable calcite precipitation occurring. Apparently, the lack of suitable nucleation sites, short residence times, and the presence of calcite inhibiting organic matter on the river sediments did not allow for calcite precipitation.

The loss of Ca^{2+} over this reach cannot be observed in the field without referring to the data, with the lowest levels occurring in the second farm dam (S4). Data also infers the possibility of calcite precipitation on the bottom sediments of the second farm dam (S4), although this was not investigated.

Sites S6-S10

The diffuse discharge carbonate spring at S6 is identified from the high Ca^{2+}, high HCO_3^- and low pH. Data suggests CO_2 degasses from solution as Davys Creek flows downstream to S8, where Ca^{2+} and HCO_3^- levels increase due to spring recharge. Spring water emerging at S8 had similar hydrogeochemistry to springs at S1 and S6 during each monitoring period (refer Figures 3,4 &5)4).

Although Ca^{2+} and HCO_3^- concentrations fall between S6 and S8, due to degassing, there is no observed evidence of calcite precipitation. Davys Creek has a relatively low gradient between S6 and S8, with sediment dams forming around mature Salix spp. Grasses and aquatic vegetation inhabit the channel between S6 and S8 with creek flow travelling below the sediment during drier periods. The gradient between S8 and S10 increases markedly (refer Figure 2). CO_2 loss is caused by an increase in hydrological agitation and is reflected in the decreasing HCO_3^-. The relatively sharp decline in Ca^{2+} and HCO_3^- concentrations between S9 and S10 coincide with tufa deposition along this reach. The largest tufa deposit in the second evolutionary segment is located several metres upstream of S10, and is a consequence of enhanced degassing. Degassing is enhanced by the increased gradient, causing the formation of tufa barrages that further disperse flow as to increase the surface area exposed to the atmosphere.

On two occasions (March 1999 and February 2000) the HCO_3^- at S11 unexpectedly increased, while there was no increase in Ca^{2+} during the same periods. The increase in dissolved CO_2 (HCO_3^-) from S10 to S11 is attributed to thick vegetation, with dissolved CO_2 recharge due to root zone respiration and long residence times. Mature Salix trees and several species of aquatic plants are present along this reach, and appear to thrive with the existing perennial flow. Sediment deposition occurs around the bases of Salix spp, with flow appearing to travel through sediment, and the root respiration zone of the existing vegetation. Observations and hydrogeochemical data suggest the influence of biogenic activity in Davys Creek can be quite substantial, although it was not investigated in this study.

Between S11 and S13 Davys Creek sank, or was pooled. S12 was deemed to be the likely dominant stream sink conduit, due to its location on a fault line. Fault lines are planes of weakness and are usually the largest conduits of sub-surface flow in karst landscapes (Gillieson, 1996). During the monitoring period, the shallow, dispersed nature of surface flow along this reach promoted CO_2 degassing, and was assumed to be the dominant process in CO_2 exsolution.

Sites S14-S19

The third evolutionary segment of carbonate spring waters starts approximately 400 metres from where Davys Creek sinks at S12. Springs emerging at S14 are saturated with Ca^{2+} and dissolved CO_2 and display a typical downstream trend in calcite precipitating streams. The rapid loss in Ca^{2+} and dissolved CO_2 between S16 and S18 is initiated by the increased hydrological agitation down this steeper reach.

The largest tufa deposit in Davys Creek is found at S17. The S16 to S17 reach consistently loses more dissolved CO_2 and Ca^{2+}, over the shortest distance, than any other reach in this study. Tufa deposition occurs at sites of hydrological agitation and is consistent with previous research (Herman &Lorah, 1988; Hoffer-French & Lorah, 1989).

Water flows over tufa barrages and dams with degassing being enhanced by this increased agitation. From S17 onwards the surface flow of Davys Creek fans out into a sediment and vegetation filled region before narrowing again at S18. During the warmer months, grasses, lilies, and a multitude of weeds and small shrubs clog this reach of Davys Creek.

The gradient increases from S18 to S19 with degassing of CO_2 due to the atmospheric gradient deemed to be the dominant process in determining the downstream change in hydrogeochemistry. The combination of low flow and large exposed surface area of the channel both promoted degassing.

SEASONAL VARIATION

The consistency of the downstream trends observed infer that similar hydrogeochemical processes operate throughout the year. The downstream variation in temperature between S1 and S13 was no more than 4°C during any one monitoring period. The major variation observed is the seasonal difference between spring sites on the Walli Andesite, and those on the limestone. The seasonal variation in temperature was found to be large enough (on average 7-20°C) to infer that source waters for springs in the first two evolutionary segments experience short residence times. Seasonal temperatures of spring waters at S1, S6 and S8 appear to be indicative of the atmospheric temperature at the time of sampling.

In contrast, seasonal temperatures at S14 ranged between 16°C and 17°C throughout the year. It is known that cave systems have ambient air temperatures that relate to the annual average atmospheric temperature (Harmon *et al*, 1978), and it was assumed that a well-developed conduit system existed under the limestone in the third evolutionary segment.

The lack of variation in seasonal temperature at S14 means that source waters have been in contact long enough to equilibrate with the temperature of the underlying conduit/cave system. This is particularly evident in July 1999, when spring sites in the first two segments registered a temperature of approximately 6°C, compared to 16°C at S14.

Research by McDonald (2000) in a local cave (Murder Cave) found the air temperature to be 16.2 °C, which is in almost perfect agreement with seasonal temperature data for S14. Also, the larger downstream variation in atmospheric temperature in the third evolutionary segment is a result of ground waters trying to equilibrate with surface temperatures, and confirms the short response time to temperature in Davys Creek.

As temperature governs the processes described in Davys Creek, it is no surprise to find that dissolved CO_2 and Ca^{2+} are also affected. On close examination it can be seen that seasonal trends are basically similar, but are raised or lowered with respect to the seasonal temperature variation observed.

In the case of HCO_3^-, it has been shown that lower temperatures allow for greater solubility of dissolved CO_2 (Lucas, 2000), hence the downstream HCO_3^- trend for the coldest monitoring period (July 1999) is generally higher than other months. With Ca^{2+} concentrations the variation is not as pronounced, but the trend is similar in calcite precipitating regions (S8-S10 and S15-S18).

CALCITE PRECIPITATION (S8-S10 and S15-S17)

The calcite-saturated ground waters feeding Davys Creek have a propensity to precipitate calcite at specific sites. These sites were recognised in the downstream trends observed, as well as visual confirmation. Only two of the three evolutionary segments identified undergo tufa deposition. Of interest is the fact that tufa deposition between S8 and S10 occurs on the Walli Andesite, which is quite uncommon.

Between S8 and S10, a series of tufa barrages ranging between 0.01 and 1 metre were observed. The average gradient along this reach was 0.03 m/m, with significant hydrological agitation being observed. Tufa deposits at the lower end of this reach were larger than the ones observed near S8, and can be seen in the steeper decline in seasonal Ca^{2+} concentrations between S9 and S10. This is in agreement with tufa deposition occurring further from the spring source (Herman & Lorah, 1987).

Average Ca^{2+} loss between S8 and S10 (~ 1.5 km in distance) ranged from 11 mg/L in July 1999 to 48 mg/L in February 2000. In March 1999 and July 1999, this reach lost 25 mg/l and 14 mg/L respectively. The large variation infers a preference for tufa deposition in the warmer months, when degassing and plant respiration are at a maximum. This preference is related to the seasonal temperature fluctuation in ground waters feeding Davys Creek, especially at S6.

The rate of Ca^{2+} loss in October 1999 has diminished in terms of the slope of the trend line observed and was attributed to the recorded, relatively larger, total monthly rainfall. This would have had a dilution effect from dam and surface runoff, thus decreasing the rate of tufa deposition. Note that hydrological agitation was assumed constant throughout the monitoring period.

In the third evolutionary segment, between S15 and S17, a similar trend is observed. The relatively constant seasonal temperatures recorded at S14 proved that source waters were in contact with limestone for a long enough time to equilibrate to conduit temperature conditions. Due to the lack of variation in the temperature of source waters for the calcite precipitating reach between S15 and S17, the seasonal downstream trends are almost identical.

The rate of Ca^{2+} loss ranges from 26 mg/L in February 2000 to 44 mg/L in March 1999. In July 1999 and October 1999, 32 mg/L and 34 mg/L of Ca^{2+} were lost respectively. The relatively small variation in downstream seasonal temperature, with the exception of May 1999, infers a relatively uniform tufa deposition rate. Including May 1999, and under assumed constant hydrological agitation, tufa deposition shows little seasonal preference along this reach.

CONCLUSION

Spring waters that source Davys Creek exhibit a significant change in their hydrogeochemistry as they flow downstream. Due to equilibrium shifts in the $CO_2/H_2O/CaCO_3$ system, the ability of flowing spring water to maintain the dissolved Ca^{2+} load is decreased (increasing the SI_c), resulting in calcite precipitation. The gradient of the creek channel enhances stream turbulence, further favouring calcite precipitation at these sites. It appears that the greater the rate of CO_2 exsolution, over the shortest downstream distance, will be the most probable site of calcite precipitation.

The seasonal temperature variation of spring waters, in the upper two segments, is large enough to infer low residence times in the aquifer sourcing these springs (S1, S6, and S8). This is implied from the similarity of atmospheric temperatures to those of the samples taken. The seasonal preference for calcite precipitation in the S8-S10 reach is purely dependent on the solubility of calcite, over a range of temperatures (Dreybrodt, 1988). Results show the larger the range in seasonal temperature, the larger the deficit between summer and winter calcite precipitation.

References:

Clesceri, L.S; Greenberg, A.E; Eaton, A.D. (editors) (1998) *Standard Methods for the Examination of Water and Wastewater, 20th Ed*, American Public Health Association (APHA), Washington DC.

Drake, J.J (1983), The effects of geomorphology and seasonality on the chemistry of carbonate groundwater, *Journal of Hydrology*, 61, pp223-236.

Dreybrodt, W. (1988) *Processes in Karst Systems: physics, chemistry, and geology*. Springer-Verlag, 228pp.

Dreybrodt, W., Lauckner, J.; Liu Zaihua.; Svensson, U., and Buhman, D. (1996), The kinetics of the reaction $CO_2 + H_2O - H^+ + HCO_3$- as one of the rate limiting steps for the dissolution of calcite in the system $H_2O - CO_2 - CaCO_3$, *Geochima et Cosmochimica Acta*, 60, pp3375- 3381.

Drysdale, R.N., and Gale, S.J. (1997) The Indarri falls Dam, Lawn Hill Creek, Northwest Queensland, Australia, *Earth Surface Processes and Landforms*, 22, pp413-418.

Drysdale, R.N., Gale, S.J., Scherrer, N.C and Fischer, M.J. (1998) The chemistry of karst waters, northeastern Barkley Tableland, northwest Queensland. In Comben, L, Long, S. and Berg, K. (eds) *Musselbrook Scientific Report,* Geography Monograph Series 4, RGSQ, Brisbane, pp97-124.

Ford, T.D. (1989) Tufa - the Whole Dam Story, *Cave Science*, 16, No2, pp39-49.

Ford, D.C. (1992) *Karst Geomorphology and Hydrology*. Chapman & Hall, Melbourne.

Ford, T.D.,and Pedley, H.M. (1996) A review of tufa and travertine deposits of the world, *Earth Science Reviews*, 41, pp117-175.

Gillieson, G.S. (1996) *Caves*. Blackwell, Oxford, pp68-76.

Harmon, R.S., Schwarcz, H.P., & Ford, D.C. (1978) Satble Isotope Geochemistry of Speleothems and Cave Waters from The Flint Ridge - Mammoth Cave System, Kentucky: Implications for Terrestrial Climate Change During the Period 230,000 to 100,000 Years B.P. *Journal of Geology*, 86, pp373-384

Herman, J.S and Lorah, M.M. (1988) Calcite precipitation rates in the field: Measurement and prediction for a travertine-depositing stream, *Geochima et Cosmochimica Acta*, 52, pp2347-2355.

Herman, J.S and Lorah, M.M. (1987) CO_2 outgassing and calcite precipitation in Falling Spring Creek, Virginia, USA, *Chemical Geology*, 62, pp251-262.

Hill, W.L. (1999) *A Report on an Examination of Dryland Salinity Processes on Three Central West New South Wales Farms*. Masters Thesis, Faculty of Sciences, University of New England, NSW, Australia.

Hoffer-French, K.J., and Herman, J.S. (1989) Evaluation of Hydrological and Biological Influences on CO_2 Flux from a Karst System, *Journal of Hydrology*, 108, pp189-212.

Jennings, J.N. (1985) *Karst Geomorphology*, Basil Blackwell, Oxford, pp1-7, 19-25, 34-69.

Langmuir, D. (1997) *Aqueous Environmental Geochemistry*. Prentice Hall: New Jersey. pp193-230.

Liu Zaihua, Svensson, U., Dreybrodt, W., Yuan Daoxian, and Buhman, D. (1995),Hydrodynamic control of inorganic calcite precipitation in Huanlong Ravine, China: Field measurements and theoretical prediction of deposition rates, *Geochima et Cosmochimica Acta*, 59, pp3087-3097.

Liu Zaihua and Dreybrodt, W. (1997) Dissolution kinetics of calcium carbonate mineral in H_2O - CO_2 solutions in turbulent flow: The role of the diffusion boundary layer and the slow reaction $CO_2 + H_2O \rightarrow H^+ + HCO_3^-$. *Geochima et Cosmochimica Acta.*, 61, 2879-2889.

Lorah, M.M., and Herman, J.S. (1988) The Chemical Evolution of a Travertine-Depositing Stream: Geochemical Process and Mass Transfer Reactions. *Water Resources Research*, 24, pp1541-1552.

Lucas, S.A. (2000) *The Downstream Hydrogeochemistry of Carbonate Spring Waters in Davys Creek, central NSW*. Honours Thesis, School of Geosciences, University of Newcastle, Aus.

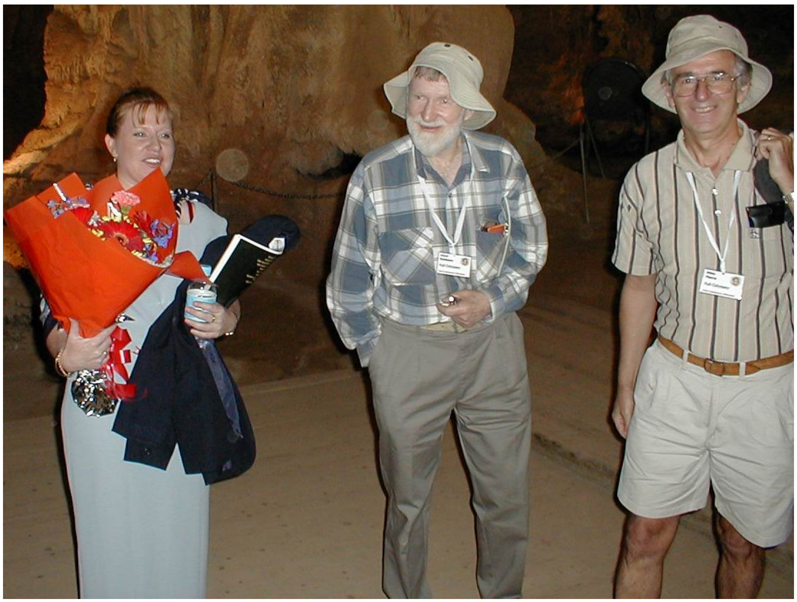
McDonald, J. (2000) *Late Quarternary Paleoclimate Reconstruction of Central N.S.W. as inferred from stable Isotope and Trace Element Geochemistry of Speleothems,* Honours Thesis, University of Newcastle, Aus.

Saurez, D.L. (1983) Calcite saturation and precipitation kinetics in the lower Colorado River, All-American Canal and East Highland Canal. *Water Resources Research*, 19, 653-661.

Stumm, W. and Morgan, J.J. (1980) *Aquatic Chemistry*, 3rd Ed. John Wiley and Sons, New York. pp1022.

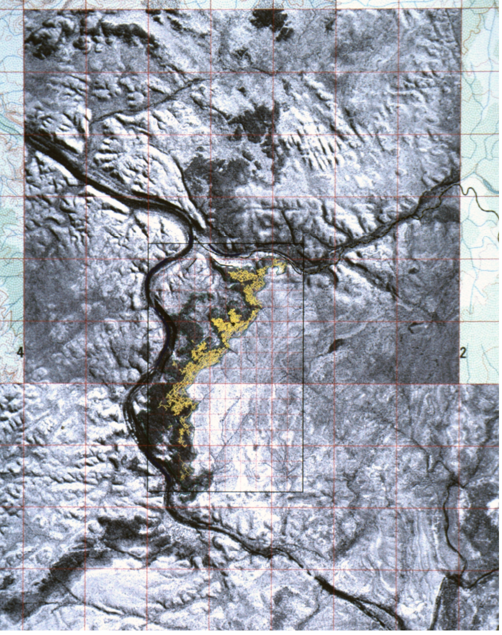
Webby, B.D. and Packham, G.H, (1982) Stratigraphy and regional setting of the Cliefden Caves Limestone Group (Late Ordovician), central-western New South Wales. *Journal of the Geological Society of Australia*, 29, pp297-317.

White, W.B. (1988) *Geomorphology and Hydrology of Karst Terrains.* Oxford University Press: New York.



Arthur Clarke

Domino, Lloyd Robinson and Miles Pierce at Conference opening at Abercrombie Caves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