

Groundwater and surface water interaction at Lake George, New South Wales

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Lake George is a fluctuating closed lake in the eastern highlands of Australia. Groundwater in the 932 km² catchment is mainly of low salinity, but high salinity groundwater is evident beneath the lake bed. Porewater analyses reveal a salinity profile in a clay aquitard 50 m thick, beneath the lake bed, that has the characteristics of diffusion but is also influenced by mixing with (a) lakewaters infiltrating downwards, and (b) groundwaters rising upwards under pressure. Hydrostatic balance is apparently achieved at a depth of 10 m below the lake bed; this coincides with the maximum porewater salinity of 40–42 000 mg/L total dissolved solids (TDS). Salt accumulates in lake-full periods and concentrates by evaporation of lake waters. A net loss of salt is evident in recessive phases of the lake. During drying and refilling episodes, the lake water surface becomes the water table and vice versa. Salt is concentrated in the capillary zone during dry periods and is also transmitted downwards by diffusion. In recessive phases there is infiltration of lake water which has a freshening effect on the top of the salinity profile, but also transmits some salt. The processes of salt accumulation and diffusion in the aquitard may have operated for much of the Quaternary. In the Lake George basin, five types of water are characterised: surface water in creeks and in the lake; groundwater in the catchment, and in sandy aquifers beneath the lake and bed; and porewater in the clay aquitard underlying the lake bed. Creek water and catchment groundwater is fresh to brackish and generally of the

$\text{HCO}_3\text{-Cl}$ or Cl-HCO_3 type with Na and Mg as major cations. The lake water is alkaline, of varying salinity up to 45 000 mg/L TDS, and of the Cl-Na type. Varying ionic concentrations in these waters are the result of evaporative concentration and precipitation of carbonate minerals. Beneath the lake bed are saline aquifer groundwaters (up to 48 000 mg/L TDS) and aquitard porewaters (up to 42 000 mg/L TDS); these are Cl-Na waters with appreciable Mg. Sulphate is also retained in the groundwater which evolves chemically through interaction with the aquifer matrix. Hydrochemical evolutionary pathways are different for groundwaters and for surface waters. In surface waters (creek and lake), dolomite and calcite saturation is achieved early but these waters are undersaturated with gypsum. In the groundwaters (catchment and lake bed), saturation with dolomite and calcite is achieved early but equilibrium relationships are more complex. Shallow groundwaters, down to 15 m beneath the lake bed, show evidence of mixing with infiltrating lake waters, and this has retarded mineral precipitation. The deeper, saline groundwaters are close to saturation with gypsum. Stable isotope data also indicate mixing down to 15 m below the lake bed between evaporated lake waters infiltrating downwards and saline groundwaters under upwards pressure. Chlorine-36 determinations indicate that younger groundwaters at 10–50 m below the lake bed overlie groundwaters at 100 m that are tens of thousands of years old.

'These are much deeper waters than I had thought'

A. Conan Doyle

The Reigate Squires, in Memoirs of Sherlock Holmes,
1888

Introduction

In much of Australia, the antiquity of the landscape has led to deep weathering and the availability of salt which has increasingly been released as a result of climatic and anthropogenic change. Thus, problems of land and stream salinity are developing on a large scale in many catchments. The interaction of groundwater and surface water is an important factor in the transport and accumulation of salt (Macumber, 1983) but the processes are not fully understood. Terminal lake basins are sites of salt accumulation, both natural and human-induced. Lake George is an example of a temperate zone, fluctuating closed lake with varying salinity. It can be considered as a natural analogue for a wastewater disposal basin, and its groundwater system may throw light on the prospects for long term hydrogeological safety of such basins.

The Lake George drainage basin is an elongate, north-south basin of 932 km² within the Southern Tablelands of New South Wales (Fig. 1). The lake itself is at latitude 35°05'S and longitude 149°25'E, about 40 km northeast of Canberra and about 100 km inland. The lake is closed and fluctuating, containing water for

85–90% of the time; the fluctuations, documented since 1820, have a period of about a decade (Fig. 2), with a maximum lake depth of 7 m. BMR has monitored lake levels and salinity on a monthly basis since 1958 (Jacobson & Schuett, 1979).

The decade of the 1980s was generally dry in southeast Australia, and Lake George was mostly dry. This enabled the investigation of the geology beneath the lake bed (Abell, 1985), with the drilling of several stratigraphic holes, undertaken in conjunction with geological mapping of the catchment (Abell, in press). In 1987 several additional holes were drilled in the lake bed, to establish the nature of the groundwater regime and ascertain its relationship to that of the catchment. Piezometer nests were established at two sites in the lake bed, 353 and 355 (Fig. 3), to depths of 10 m, 55 m and 100 m at each site. A shallow (2 m) piezometer was installed at site 351. Drillholes were cored at two other locations, 352 and 354, to allow the extraction of porewaters for determination of chemistry and porosity. The selected transect is considered to be representative of conditions under the lake bed.

The interaction of groundwater and surface water at Lake George has been the subject of speculation. A considerable loss of dissolved salt has been observed during recessive phases of the lake (Jacobson & Schuett, 1979) and attributed to wind deflation of precipitated salts. Transfer of salts from surface water to groundwater during seiches has been suggested as a possible cause (Torgersen, 1984). Bowler (1986) suggested that the porewaters may act as a storage system for salt transferred from surface waters. This report outlines the hydrogeology of the Lake George basin and clarifies the processes involved in the interaction of the groundwater and surface water systems.

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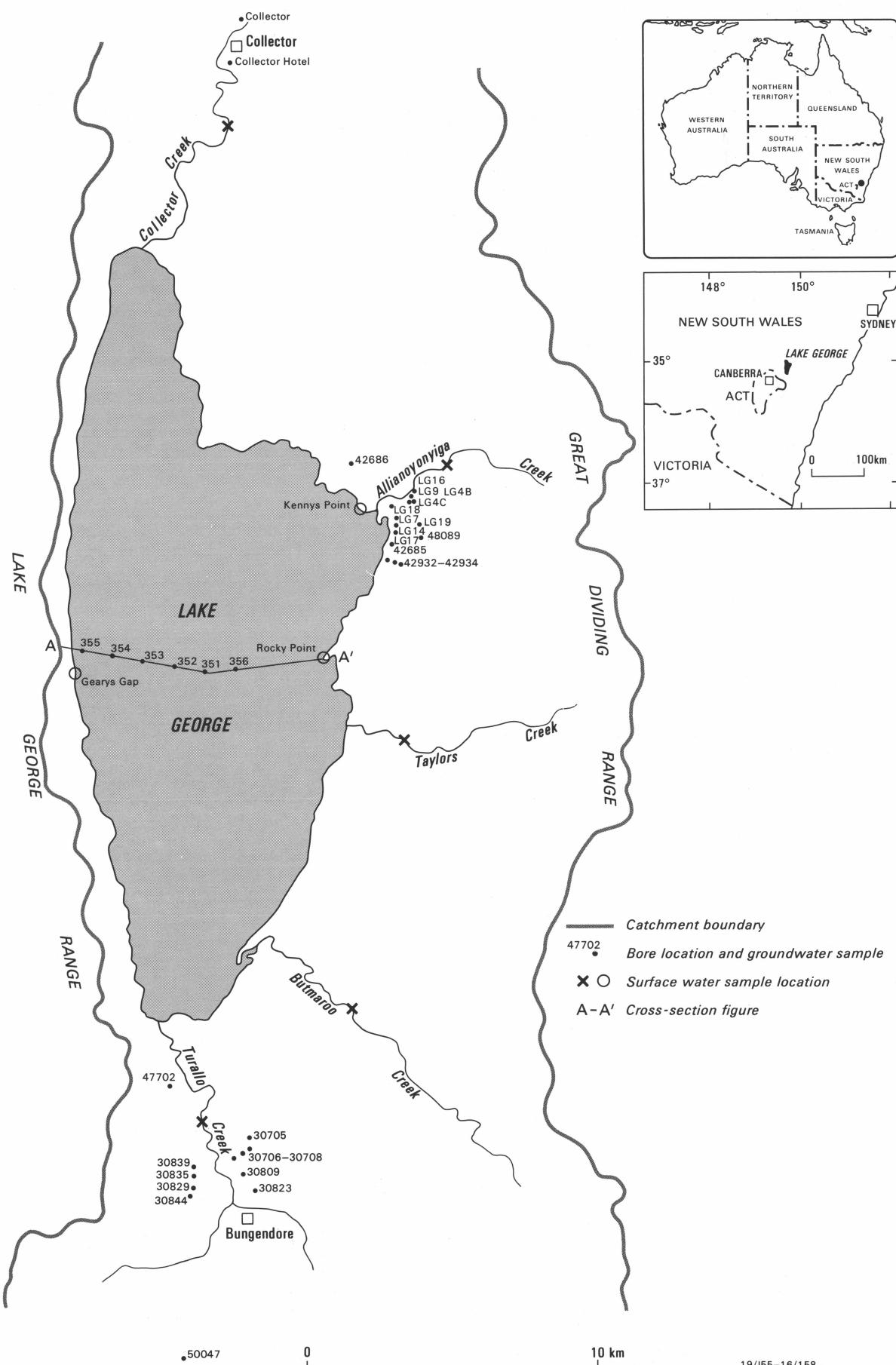


Figure 1. Location map.

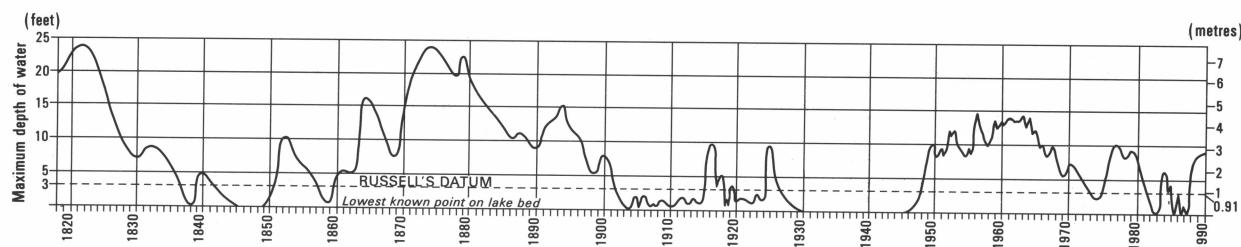


Figure 2. Fluctuations in water level, Lake George, 1819–1990.

Geology and physiography

The geology of the catchment is shown in Figure 4. The pre-Cainozoic, bedrock geology comprises marine sedimentary rocks of Middle to Upper Ordovician age, which are overlain unconformably by late Silurian volcanic rocks and intruded by Siluro-Devonian granite. The sequence was folded, faulted and weakly metamorphosed by a series of Palaeozoic earth movements which gave a meridional trend to the geological structure. After Permian time the region remained sufficiently stable for an ancient landscape to develop by the Late Cretaceous.

In the mid-Tertiary, the Lake George basin originated by faulting, possibly by the rejuvenation of late Palaeozoic faults (Abell, 1985). The Cainozoic sediments were deposited in a normal fault-angle basin. Sedimentary events have been dated from Quaternary and Tertiary pollen (Truswell, 1984; Singh & Geissler, 1985) and from a palaeomagnetic profile dating back at least to the Pliocene (Singh & others, 1981; Mason, 1987).

Beneath Lake George, drilling has revealed the existence of more than 150 m of fluvio-lacustrine sediments. This has enabled the Cainozoic sequence in the basin to be divided into three lithostratigraphic units: the Geary's Gap Formation, the Ondyong Point Formation, and the Bungendore Formation (Fig. 5). The Geary's Gap Formation consists of deeply weathered fluvial sand and gravel. These early Tertiary sediments were deposited unconformably on Palaeozoic bedrock, and are associated with a prior drainage system which was incised into bedrock and flowed northwest. Palaeochannels can be traced under the lake bed (Abell, 1985). The Ondyong Point Formation consists of fluvial sand and lacustrine clay and silt deposited disconformably on deeply weathered sediments. The Bungendore Formation comprises lacustrine clay and silt; it is conformable on the Ondyong Point Formation and separated from it by a laterally persistent layer of sand and silt. The latter two units represent deposition in a closed drainage basin and their lithofacies is largely a function of climatic change.

A complex clay-mineral assemblage has been identified in the Cainozoic sequence (Abell & others, 1985). Calcite and dolomite also occur in small quantities throughout the sediments. Gypsum occurs in the upper part of the Bungendore Formation and at its lower boundary with the Ondyong Point Formation. Traces of halite occur in both the Bungendore Formation and Ondyong Point Formation. These minerals are considered to be authigenic.

Quaternary sediments in the basin include colluvial deposits on the flanks of hills and along the Lake George escarpment, and lacustrine strandline and aeolian deposits around the lake margins. Ancient strandlines up to 37 m above the lake bed testify to very large fluctuations of water level in late Quaternary time. Above this elevation the lake overflowed through Geary's Gap into the Yass River drainage system; this last happened between 27 000 and 21 000 years B.P. (Coventry, 1976).

The Lake George basin now represents a base level of internal drainage. The basin margin is defined by the topographically subdued watershed of the Great Divide in the east, and by the Lake George Range in the west. At its northern and southern limits, the basin margin comprises subdued topography with low saddles, a complex of natural and artificial drainage lines, and swampy lagoonal areas. Within the basin, topographic relief commonly ranges from 680 to 900 m above sea level. The floor of the lake is at an elevation of about 674 m.

Streams in the basin occupy wide open valleys in their upper reaches. They converge towards Lake George by meandering across flat alluvial plains and embayments. Evidence of faultline rejuvenation disrupting the headwater system of the Yass River is indicated by elevated river gravels, the remnant of a broad valley at Geary's Gap, and the barbed drainage of creeks flowing to the northern end of Lake George (Taylor, 1907; Ollier, 1978; Abell, 1985).

The pre-European landscape of the basin consisted of wooded, eucalypt-covered terrain, relics of which still remain. Fragmentary charcoal in lake-bed sediments, and plant microfossil evidence for the expansion of eucalypts, suggest increased fire frequencies, possibly due to human activity, in the last 130 000 years (Singh & Geissler, 1985). The largely erosional present-day landscape reflects the impact of European settlement over the last 200 years. Extensive clearing of vegetation for grazing and cultivation has led to land degradation, including erosion gullying, particularly in areas blanketed by colluvial and alluvial slope deposits. The expansion of Canberra has demanded building materials, and sand and gravel are extracted from strandline and aeolian deposits around the northern and southern margins of Lake George. This has led to the deterioration of natural vegetation and landforms associated with these deposits.

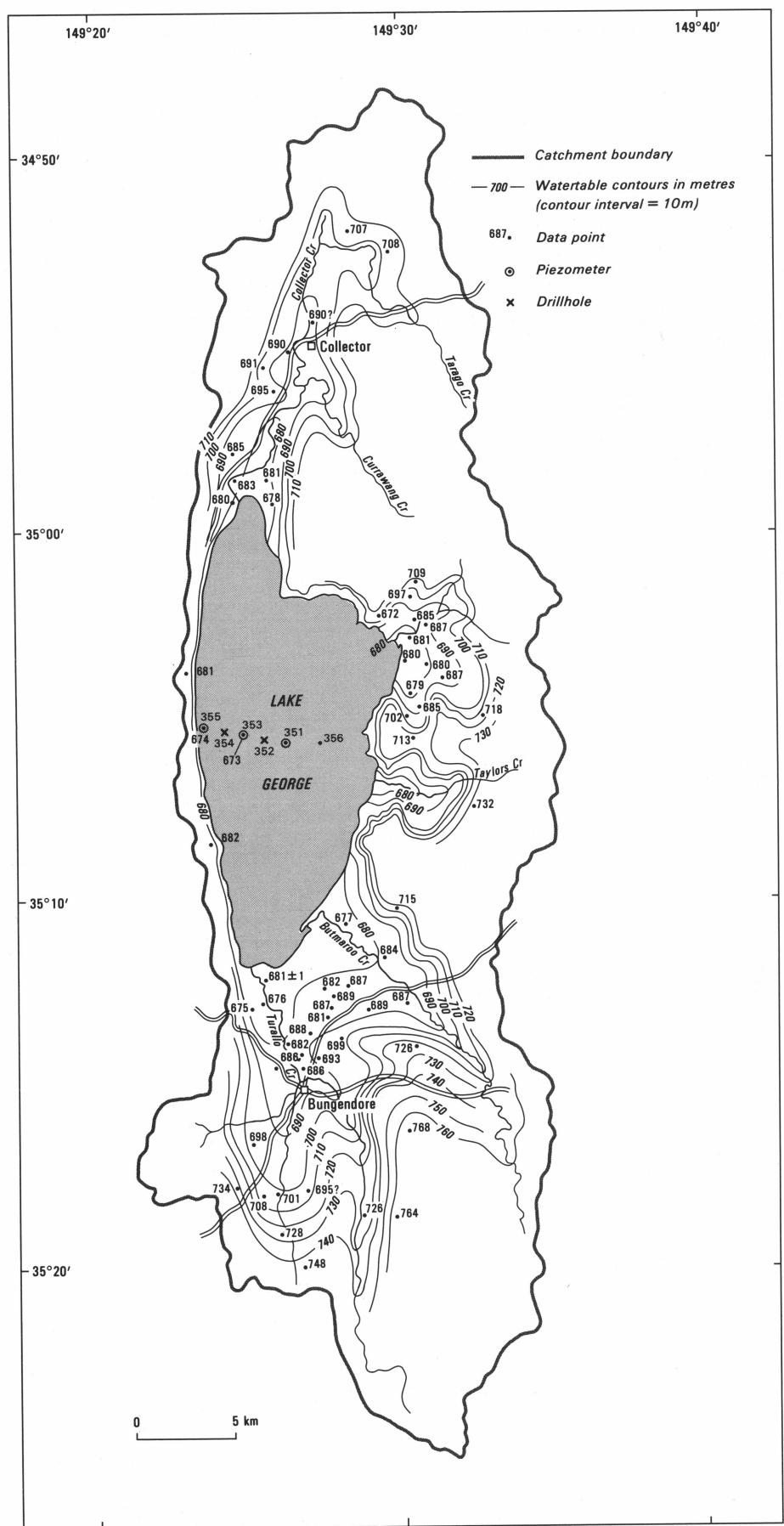


Figure 3. Potentiometry of the Lake George catchment.

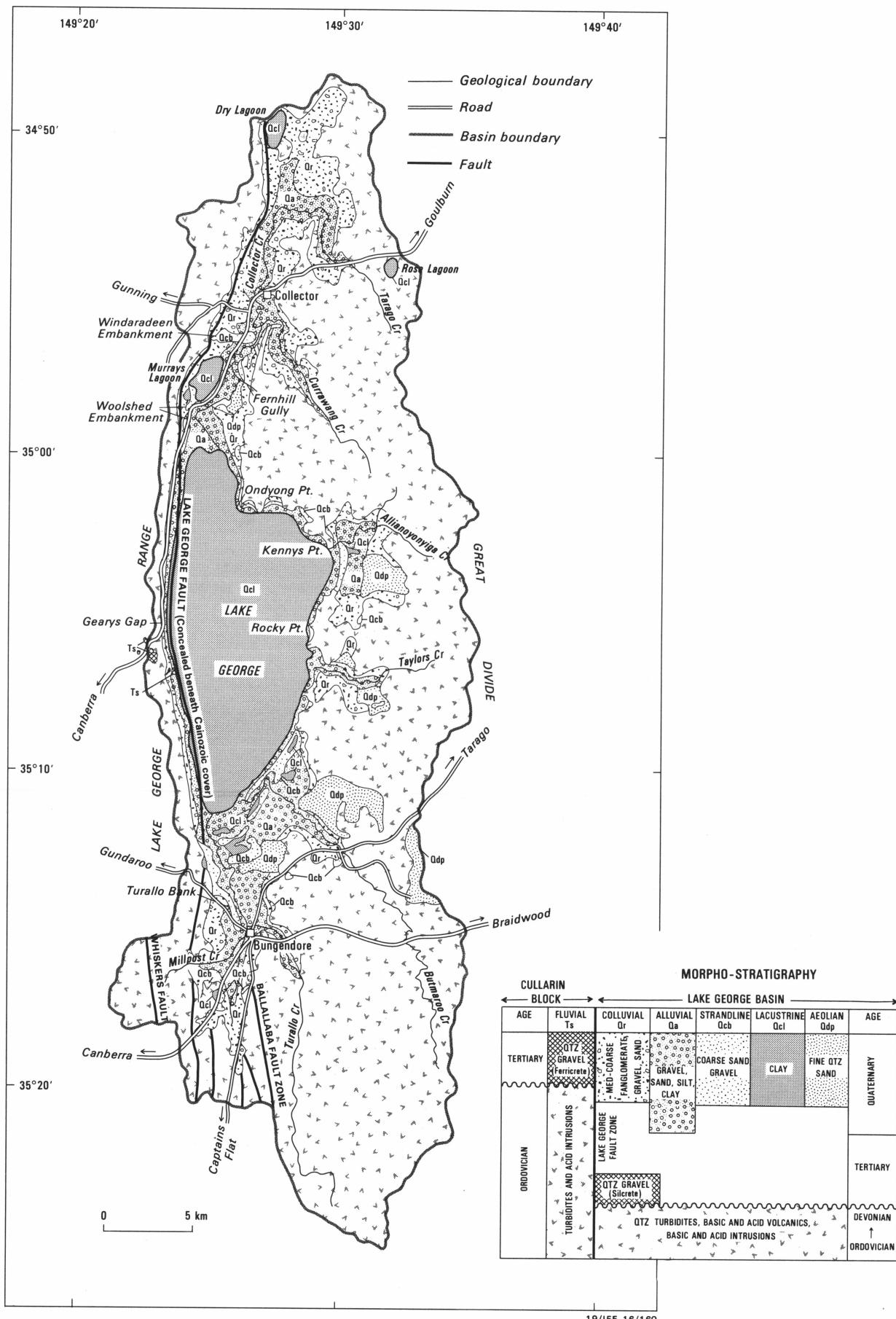


Figure 4. Geology of the Lake George catchment.

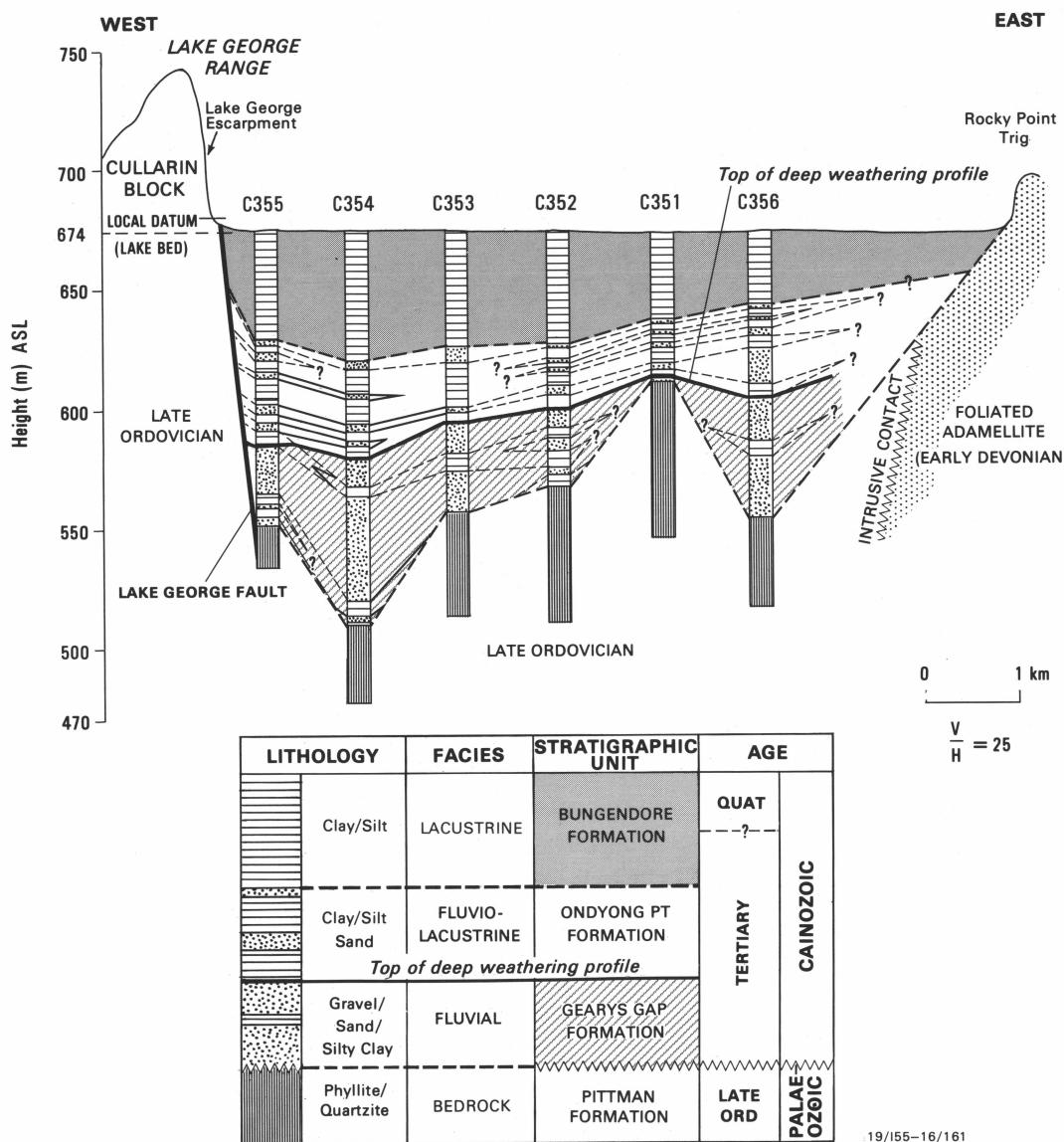


Figure 5. Cross-section of Lake George showing stratigraphy.

Climate and hydrology

The present warm temperate, continental climate over the Lake George basin is typified by hot summers and cold winters. Average monthly temperatures at lake level are: January, maximum 27°C, average 20°C, minimum 12.5°C; July, maximum 10.5°C; average 5°C, minimum -0.5°C. The effect of altitude in the catchment is to moderate the summer and lower the winter temperatures. The annual precipitation is variable: the range over a century of records is 390 mm to 1120 mm. Mean annual precipitation is estimated as 750 mm, based on records from two rain gauges in the catchment at Bungendore and Collector. Precipitation is distributed fairly evenly throughout the year with a maximum in October. Evaporation is about 1200 mm annually and occurs mainly between October and April.

Lake George constitutes about 16% of the total area of the drainage basin. Several creeks and watercourses con-

verge towards the lake: Collector Creek from the north, Allianoyonyiga, Taylor and Butmaroo Creeks from the east and Turralo Creek from the south (Fig. 3). About $50 \times 10^6 \text{ m}^3/\text{year}$ enters the lake from surface runoff.

Lake George is a shallow body of water which shows marked fluctuations in level and salinity. The lake hydrograph is one of the oldest and most continuous water level records in Australia (Russell, 1886). In historical times, changes in the regional climatic pattern have caused the lake to dry out. Over the last ten years, Lake George has dried out for a nine month period in 1982-83, and annually in 1986, 1987 and 1988. Over the last 170 years, the hydrographic record (Fig. 2) shows that the water depth in Lake George has rarely passed 6 m and has not exceeded 7.5 m. Commonly its depth is 1.5-4.5 m and its area 130-160 km².

Monitoring during lake-full periods shows that the lake

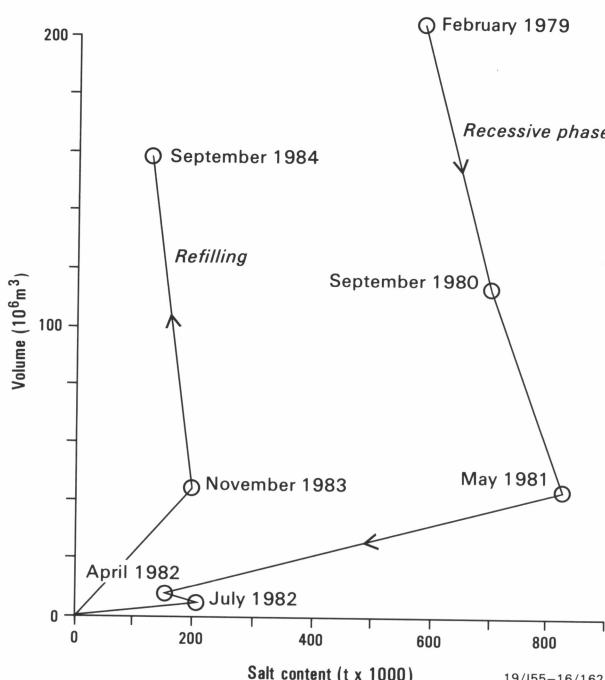


Figure 6. Loss of dissolved salt in recessive phase, 1982.

level fluctuations are a response to seasonal and long-term variations in rainfall, evaporation and inflow of streams (Jacobson & Schuett, 1979). The lake water balance shows marked seasonal characteristics. In general, increases in water volume between May and October correspond with large inflows of water and low evaporation, whereas decreases in water volume between November and April correspond with lesser inflows and high evaporation. The longer term fluctuations with a periodicity of about a decade (Fig. 2) reflect climate variability in southeast Australia, and the dry phases of Lake George correspond with economically significant, severe droughts in this region. The drying out of Lake George in 1982–83 corresponded with the major El Niño Southern Oscillation event of the century. Salinity of the lake water also fluctuates; it increases as the lake level and water volume decrease. Salinity ranges from about 400 mg/L total dissolved solids (TDS) when the lake level is 4 m and water volume is about $450 \times 10^6 \text{ m}^3$, up to 40 000–45 000 mg/L when the lake level is less than 1 m, and water volume less than $40 \times 10^6 \text{ m}^3$.

In recessive phases of the lake, such as the drying-out in 1982, a net loss of dissolved salt is observed. Thus the total dissolved salt content increased during lake recession from 600 000 t in 1979 to about 800 000 t in early 1981 (Fig. 6). This was rapidly lost during drying out when the lake level fell below a critical depth of 1 m. On refilling in 1983 the total salt content rose to 200 000 t at a lake level of 1 m.

The lake and the groundwater system are hydraulically connected when the lake fills (Fig. 7). When the lake is dry, the watertable is about 0.5 m below the surface and playa-like conditions develop. Lake water levels are subject to diurnal fluctuations, which may be up to 10 cm,

as a result of seiches. The seiches are induced by north-easterly or southerly winds spreading thin sheets of water across the lake bed (Burton, 1972). This water movement gives visible diurnal changes in water level and area, leading to increased water losses by evaporation or infiltration.

Hydrogeology

Figure 8 illustrates the dual hydrological cycle for the Lake George Basin. In the wet cycle, the lake is filled and maintained mainly by surface runoff; shallow aquifers are recharged, mainly in the winter months when rainfall exceeds evaporation (Burton, 1977). In the dry cycle, groundwater flow towards and beneath the lake discharges through capillary evaporation from the dry lake bed.

Figure 3 shows potentiometry in the catchment based on information from water bores. Groundwater flows towards Lake George in fractured rock and alluvial aquifers from the north, east and south. On the west side, the topographic divide is close to the lake; this probably coincides with the groundwater divide although potentiometric information is sparse in this area. Groundwater in sand and gravel aquifers beneath the lake bed (Gearys Gap, Ondyong Point Formation) is confined by a clay aquitard (Bungendore Formation). Recharge to the lake-bed aquifers occurs mainly in alluvial embayments at the lake margin (Fig. 9). Hydraulic continuity is assumed in this study although these aquifers are in fact shoestring sands, and considered on a detailed scale may not be continuous. The alluvial aquifers are used for water supply at the town of Bungendore and the Woodlawn mine. Throughout the catchment, fractured bedrock aquifers are used for dispersed farm and livestock water supplies.

In the alluvial aquifers north and south of the lake, the groundwater is fresh, containing 150–500 mg/L TDS. To the east, the alluvial aquifers contain 800–1500 mg/L TDS. Fractured rock aquifers in the catchment vary in salinity from 250 to 2000 mg/L TDS; this variation is ascribed to dissolution of salts in the weathered mantle and varying residence time of groundwater (Evans, 1987).

Beneath the lake bed, investigation drillholes show that 50 m of clay overlies thin sand and gravel aquifers (Fig. 9) which in turn overlie bedrock at depths of up to 160 m.

Groundwater pressures have been measured in lake boreholes. Fluctuations in groundwater level reflect the marked seasonal climatic variation in the catchment (Fig. 10) and are damped with increasing depth. These groundwaters are saline (10 000–48 000 mg/L TDS; Fig. 11), and are therefore of variable density. To allow comparison, the measured heads have been converted to equivalent freshwater heads. Upwards movement of groundwater beneath the lake bed is inferred from the head distribution, and the lake thus appears to be a zone of regional groundwater discharge. The groundwater pressure is generated by the catchment topography which is up to 200 m above Lake George.

The salinity configuration of the groundwater beneath the lake (Fig. 11) appears to be unstable, in that denser

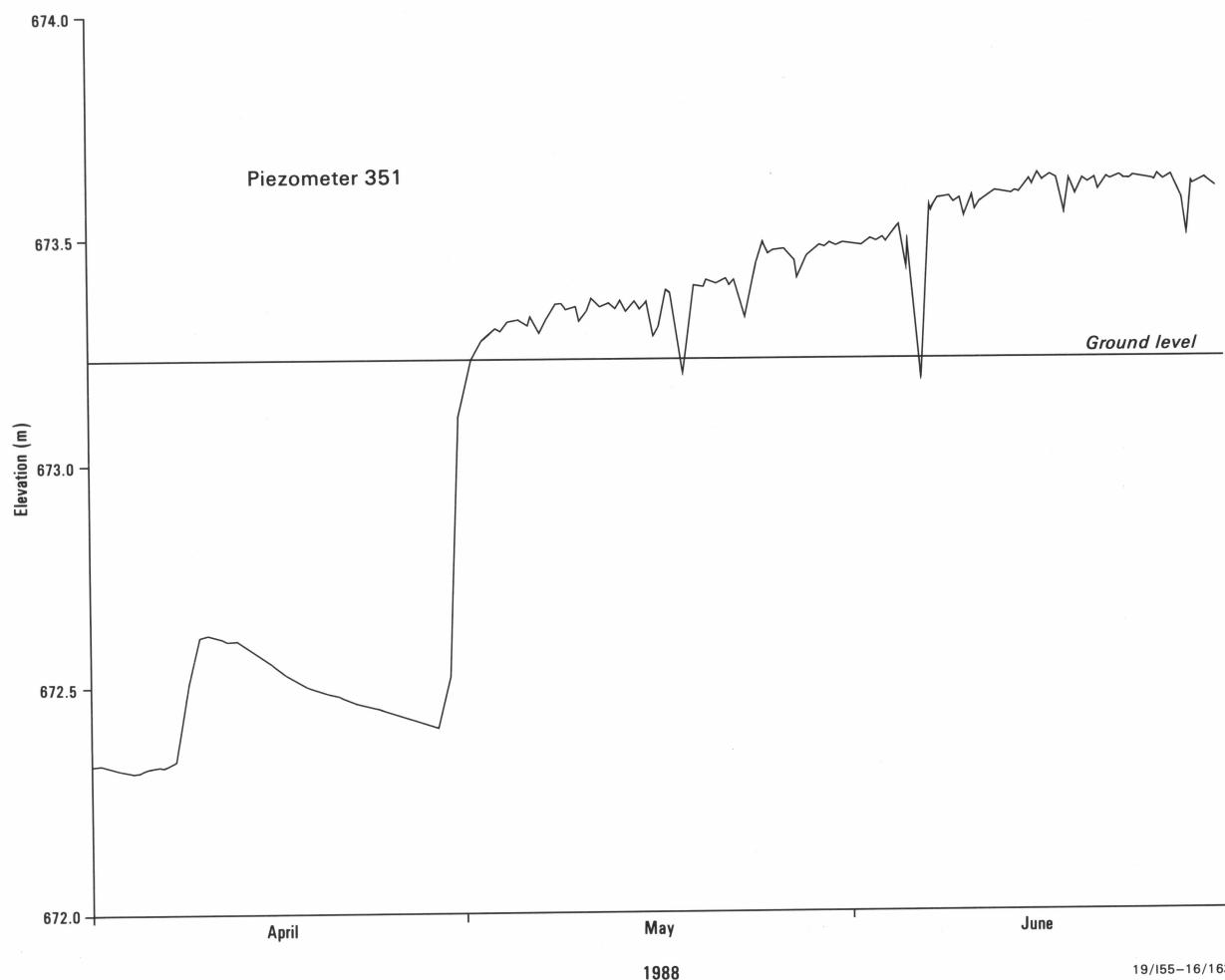


Figure 7. Lake George hydrograph, 1988, showing effects of lake filling.

water ($>40\,000 \text{ mg/L TDS}$) overlies less dense water ($10\,000 \text{ mg/L TDS}$). In this situation, whether flow of fluid actually occurs depends on the magnitude and direction of the pressure gradient. J.S. Hanor (Louisiana State University) and W.R. Evans (BMR) (personal communication, 1989) have analysed a similar case involving one-dimensional vertical fluid flow through the Geera Clay aquitard in the Murray Basin, southeast Australia. Their analysis was based on Darcy's Law, from which it can be shown that for such a density-layered system to be in hydrostatic equilibrium

$$\frac{dP}{dz} = \sigma g$$

where dP/dz is the pressure gradient, σ is fluid density, and g is the gravitational constant. For fluid flow to occur, there must be an imbalance of the pressure gradient, so that

$$\frac{dP}{dz} > \sigma g$$

for upwards flow, or

$$\frac{dP}{dz} < \sigma g$$

for downwards flow.

In order to analyse the Lake George situation, groundwater pressures in piezometers were calculated as

$$P = \sigma g L$$

where L is the vertical length of the fluid column in the piezometer. From this, the pressure driving fluid flow was calculated to be about 7500 Pa/m in the top 10 m of the profile and about $10\,000 \text{ Pa/m}$ from 10 to 100 m (Fig. 12). The pressure resisting fluid flow, due to fluid density, σg , was calculated as decreasing vertically downwards from just over $10\,000 \text{ Pa/m}$ near the surface to 9840 Pa/m at a depth of 100 m . Comparing the magnitudes of the two opposing gradients (Fig. 12), it appears that upwards flow occurs in the lower part of the section. There is hydrostatic balance at a depth of about 10 m below the lake bed, and above that level a lessening of the pressure gradient implies that downwards flow occurs.

The salinity of pore waters in the aquitard (Bungendore Formation) is shown in Figures 13 and 14. Salinity increases downwards to a maximum of $32\,000 \text{ mg/L}$ at 7 m and 12 m in bore 352, and to maxima of $42\,000 \text{ mg/L}$ at 4.5 m and $40\,000 \text{ mg/L}$ at 12.5 m in bore 354. Beneath these maxima, salinity decreases downwards, almost linearly, to $10\,000 \text{ mg/L}$ at 53 m in

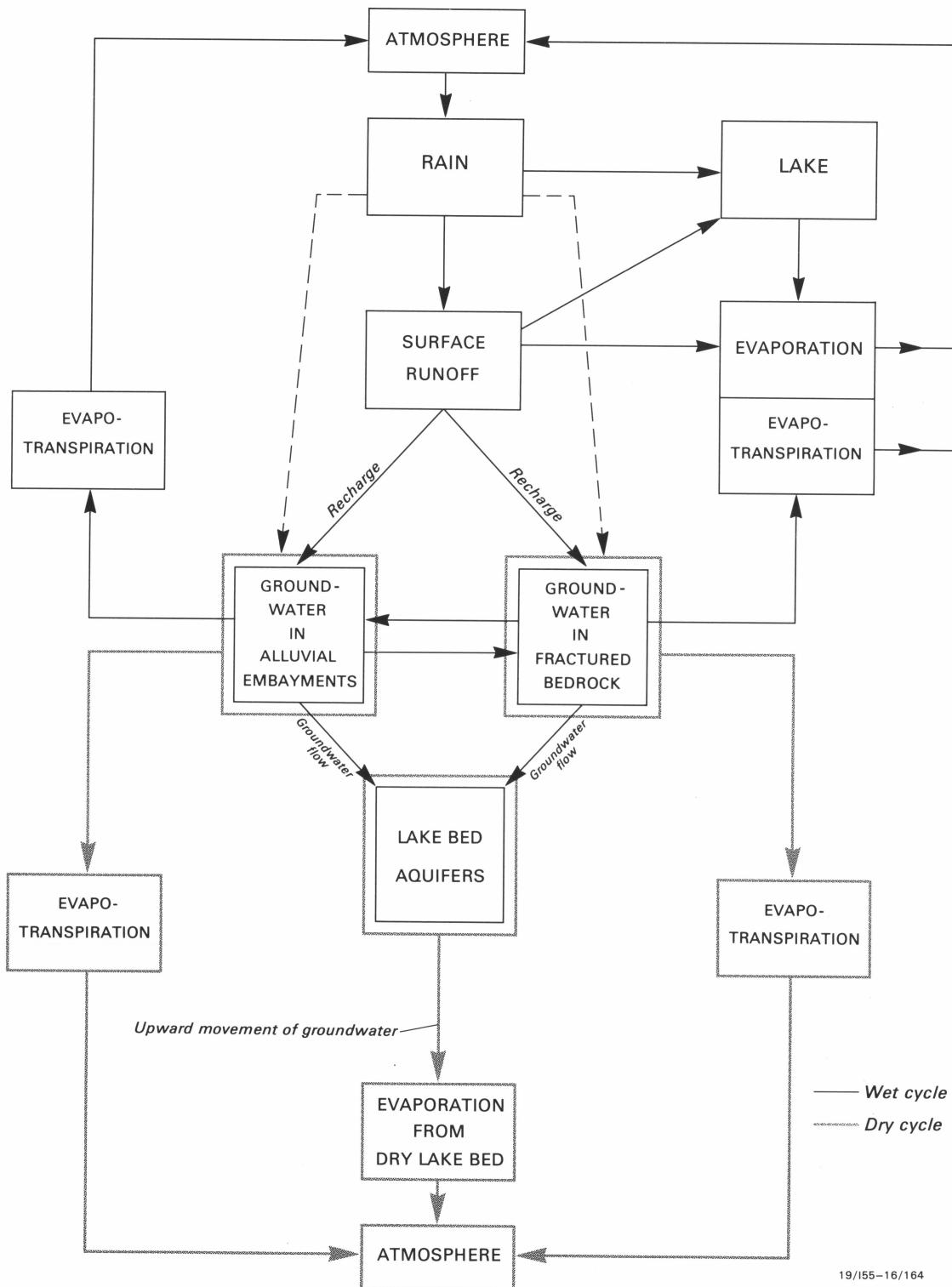


Figure 8. Hydrological cycle for the Lake George basin, showing wet and dry cycles.

352 and 18 000 mg/L at 52 m in 354. The nearly linear trend in salinity suggests diffusive transport of salt downwards. The lower salinity in the upper part of the section suggests dilution by superimposed freshwater and displacement of the diffusive profile downwards.

To estimate the diffusive flux of solute Fick's first law can be applied. According to this,

$$J = - D^\circ (\phi/\theta^2) \nabla C$$

where J is solute flux ($\text{kg}/\text{m}^2\text{s}$), D° is the diffusion coefficient in free solution (m^2/s), ϕ is porosity (m^3/m^3), θ is the resistivity formation factor, which is an index of tortuosity (m/m) and ∇C is the concentration gradient ($\text{kg}/\text{m}^3/\text{m}$). The diffusion coefficient was taken as $1.25 \times 10^{-9} \text{ m}^2/\text{sec}$ for NaCl in the appropriate concentration

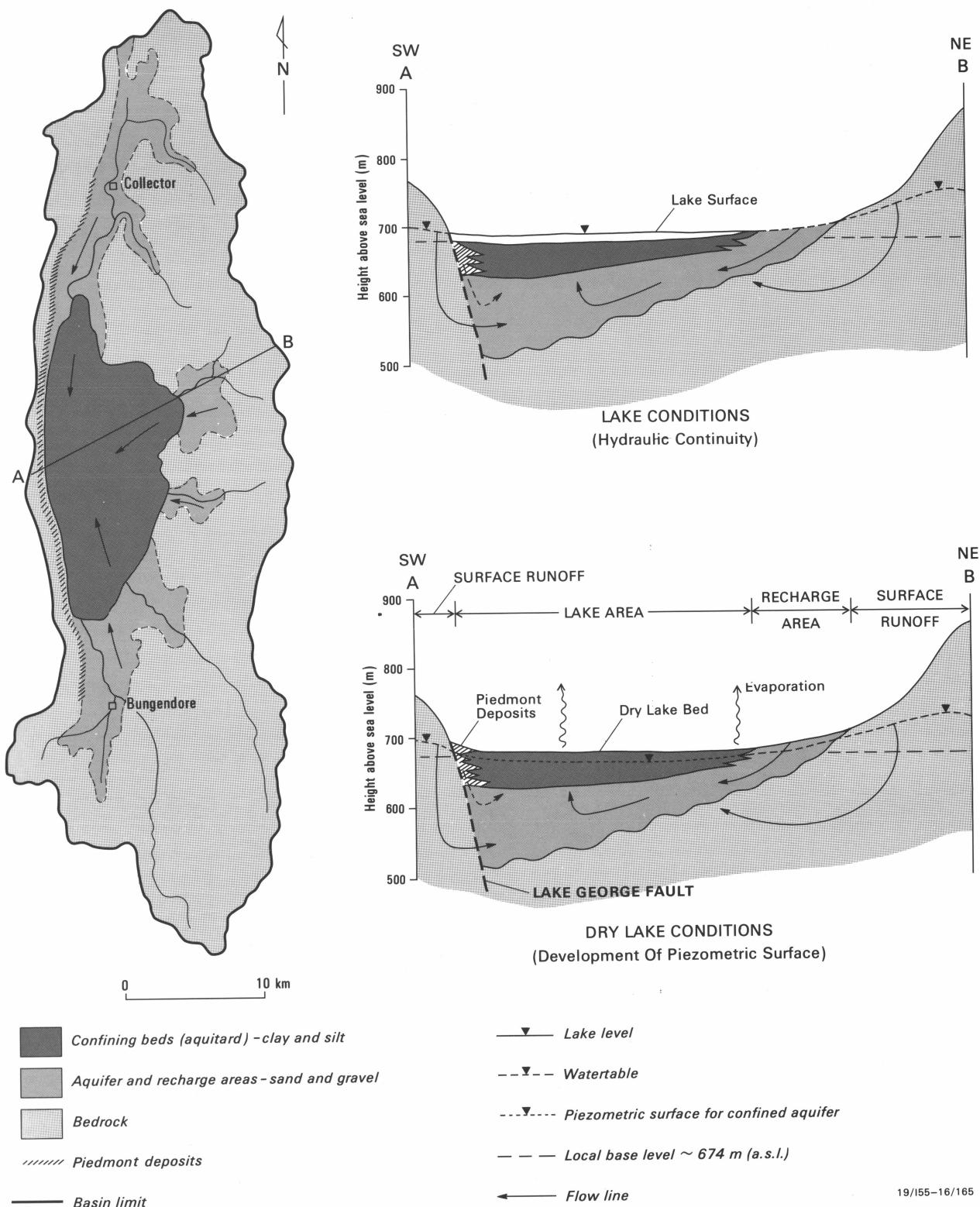


Figure 9. Hydrogeology of the Lake George basin.

range at 18°C; average porosity was estimated as 0.55 based on measurements in core samples (Figs 13, 14); the formation factor was estimated as 3.5 based on

published experimental results for sediments of similar porosity (Manheim & Waterman, 1974); and the concentration gradient was calculated as 0.172 kg/m³/m from

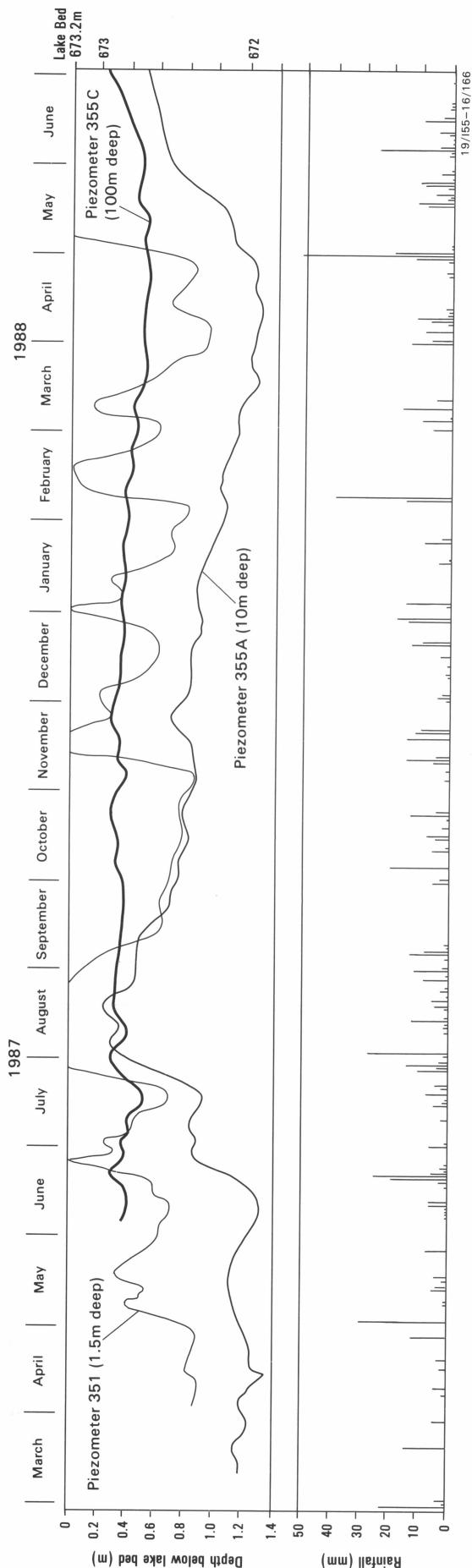


Figure 10. Fluctuations in measured potentiometric level, Lake George groundwaters.

data obtained for Na in bore 352 (Fig. 13). Substituting in the above equation, we obtain

$$\begin{aligned} J &= -(1.25 \times 10^{-9})(0.55/12.25)(0.172) \text{ kg/m}^2 \text{ s} \\ &= -3.05 \times 10^{-4} \text{ kg/m}^2 \text{ year} \end{aligned}$$

Thus the flux of dissolved NaCl downwards through the aquitard is about $0.3 \text{ g/m}^2 \text{ year}$.

The total mass of dissolved salt in the aquitard can be calculated as the product of porewater volume and salinity (Figs 13, 14) for sites 352 and 354. For 5 m sections of the aquitard, Figure 15 shows the salt distribution with depth. For a 54 m deep section in bore 352, the total salt accumulated is 549 kg for a 1 m^2 cross-sectional area, and for a 52 m deep section in bore 354 the total salt accumulated is 764 kg for a 1 m^2 cross-sectional area. Thus the average salt accumulation beneath Lake George is about 0.65 t per 53 m section per m^2 area. The total salt accumulation for the 53 m aquitard section is the product of lake area and salt accumulation, i.e. $15\ 000 \times 10^4 \times 0.65 \text{ t} = 97.5 \times 10^6 \text{ t}$. This compares with the mobile salt mass in the lake water (Fig. 6) of about 800 000 t.

Considering a 1 m^2 column of the aquitard, we find that 0.65 t of salt has accumulated, and that the present-day diffusion rate is 0.3 g/year. This implies that salt accumulated and diffused over a period of $(650\ 000/0.3)$ years, i.e. about 2×10^6 years. Porosity was probably greater in the past and there was probably an increased concentration gradient during arid periods, suggesting a somewhat greater diffusion rate at times. Nevertheless, these processes have operated in the aquitard for a considerable part of Quaternary time.

Hydrochemistry

Chemical analyses of selected samples of Lake George catchment waters are shown in Table 1. This data base has been developed over 20 years from analyses by BMR supplemented by selected analyses from files of the New South Wales Department of Water Resources. In the present investigation, lake-bed piezometers have been sampled and analysed for major ions, stable isotopes and radioisotopes.

Major ion concentrations

The hydrochemistry of surface waters is considered in terms of two groups: creek runoff water and lake water. Five creeks flow into Lake George intermittently (Fig. 3). Salinity of their water ranges from 100 to 2500 mg/L TDS, and varies with time and the amount of stream flow. The freshest creek water, from 100 to 300 mg/L TDS, is of the $\text{HCO}_3\text{-Cl-Na-Mg}$ type, creek water with 300 to 1500 mg/L TDS is generally $\text{Cl-HCO}_3\text{-Mg-Na-Ca}$ water, and more saline creek water is Cl-Na water.

The lake water varies in salinity inversely with lake stage and water volume. Figure 16 shows compositional changes as the lake level falls. The fresher lake water is of the Cl-Na type with appreciable Mg and HCO_3 . The brackish and saline lake waters are also Cl-Na waters but have greater concentrations of Cl, Na and SO_4 . With increasing lake salinity the Ca concentration in lake waters increases very slowly; the HCO_3 concentration

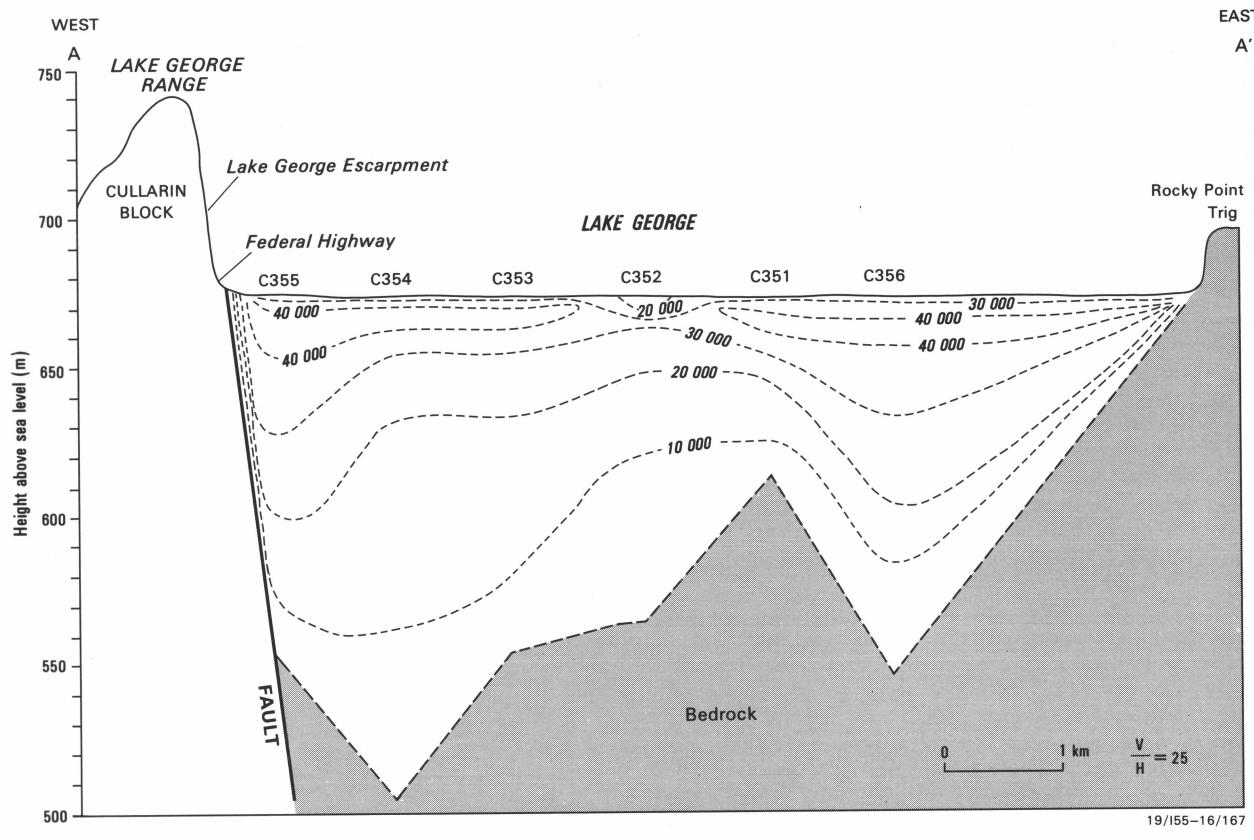


Figure 11. Distribution of salinity in lake-bed groundwaters.

increases initially then decreases in the more saline waters. With increasing salinity, the lake waters become more alkaline, with pH about 9, and contain CO_3 (Table 1).

The hydrochemistry of the groundwaters is considered in terms of three groups: catchment borewater, groundwater beneath the lake bed, and porewater in the aquitard. The catchment bores, in alluvial and fractured rock aquifers, generally contain groundwater with 150–2000 mg/L TDS. The fresher catchment groundwater, less than 200 mg/L, is of the $\text{HCO}_3\text{-Na-Mg-Ca}$ type; it becomes the $\text{HCO}_3\text{-Cl-Na-Mg-Ca}$ type in the salinity range 200–400 mg/L TDS, and the $\text{Cl-HCO}_3\text{-Na-Mg-Ca}$ type above 400 mg/L TDS. Groundwaters beneath the lake bed are brackish Cl-Na waters with appreciable SO_4 and Mg (Table 1).

The porewaters are alkaline and Cl-Na rich with appreciable SO_4 and Mg. Salinity trends are paralleled by Na and Cl concentrations, but the Mg and SO_4 concentrations show different characteristics in the two investigated sections (Figs 13, 14).

The major ion composition of surface waters and groundwaters is shown in a Piper trilinear diagram (Fig. 17). Distinctive evolutionary trends are evident. With increasing salinity, the surface waters trend towards the Cl and Na corners, reflecting the process of evaporative concentration. Groundwaters follow a more complicated pathway and trend eventually towards the SO_4 and Mg corners. Groundwaters from beneath the lake bed are distinctively grouped on Figure 17; they plot along the Cl-SO_4 side of the anion diagram, close to the Cl

corner, and along the Na-Mg side of the cation diagram, close to the Na corner. Samples from 50 and 100 m plot close to the evolutionary pathway of the catchment groundwaters, but samples from 1 and 10 m plot closer to the evolutionary pathway of the surface waters. This suggests mixing of surface waters and groundwaters beneath the lake bed and explains the high SO_4 concentrations in the waters at 10 m depth (Figs 13, 14). Sulphate is concentrated by the infiltration of lake waters and the upwards flow of groundwater, but is not taken up in precipitation as the mixed waters are undersaturated with gypsum.

Figure 18 shows relationships of the major ions Na, Mg, and Ca, with increased salinity. Surface waters and groundwaters again reveal distinctive evolutionary trends. In the lake waters, Na concentration increases along a line with 45° slope (Fig. 18a), indicating that evaporative concentration is the main process. In the catchment and lake-bed groundwaters, Na concentration also increases more or less linearly towards a maximum at a depth of 10 m beneath the lake bed. The concentration line is displaced relative to that of the lake waters, and probably represents the acquisition of Na by dissolution of stored salts in the weathered zone, and subsequently of aquifer matrix. Creek runoff waters are grouped with the catchment groundwaters in this plot, and the scatter of points reflects the variability of catchment conditions.

In the lake waters, Mg concentration increases with increasing salinity along a line with slope 45° (Fig. 18b), indicating that evaporative concentration is the main process. In the catchment groundwaters and creek runoff

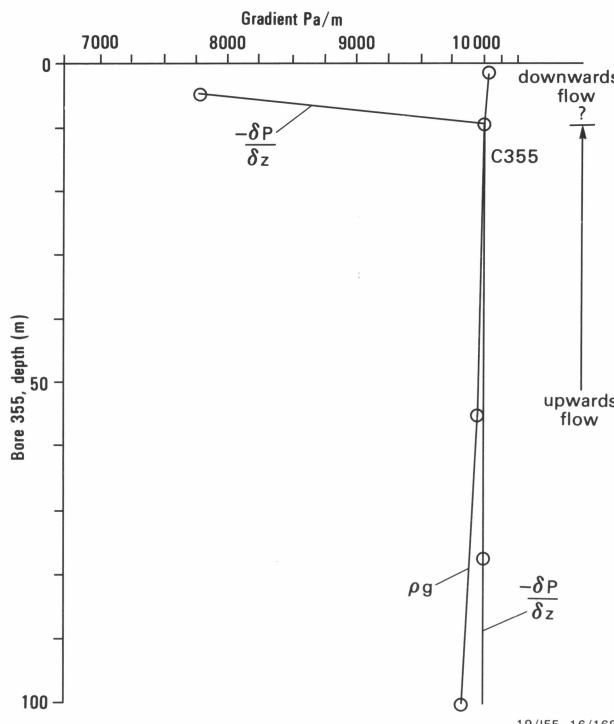


Figure 12. Comparison of pressure gradients affecting fluid flow.

waters, the Mg concentration trend is also linear but the line is displaced above that of the lake waters. Dissolution of chlorite in aquifer matrix is probably the main contributor of Mg to the groundwater system (Evans, 1987). The linear trend continues to the more saline lake bed groundwaters where the scatter of points on the plot suggests some mixing with surface waters.

The plot of Ca concentration versus salinity (Fig. 18c) is completely different. In the surface waters, Ca concentration increases until salinity reaches about 1000 mg/L TDS, probably as a result of dissolution. It then decreases slightly with further increase in salinity. This is probably due to precipitation of calcite and dolomite. In the catchment groundwaters, Ca concentration increases with increased salinity, as a result of dissolution of aquifer matrix. In the saline lake-bed groundwaters the Ca concentration again decreases, and the scatter on the plot suggests some mixing of these saline groundwaters with lake waters.

Figure 19 shows relationships of Cl, SO₄ and alkalinity concentrations with increasing salinity. The Cl concentration (Fig. 19a) increases with salinity in fresher surface waters and catchment groundwaters; the Cl is probably derived from stored salts in the weathered zone (Evans, 1987). Brackish and saline lake waters show an increase in Cl concentration with salinity, along a line with slope 45°, suggesting evaporative concentration. The SO₄ concentration (Fig. 19b) increases as salinity increases in both surface waters and groundwaters. Lake waters increase in SO₄ concentration relative to TDS along a 45° slope line, indicating evaporative concentration. In lake-bed groundwaters the SO₄ concentration increases markedly relative to TDS. This reflects both dissolution of sulphide in the aquifer matrix, and downwards diffusion of salts concentrated in shallow

groundwater under dry lake conditions. The alkalinity (Fig. 19c) generally increases with salinity in fresher surface waters and groundwaters. Both trends flatten off at about 1000 mg/L TDS due to precipitation of carbonate minerals. In the lake waters, increasing salinity beyond 1000 mg/L TDS parallels increased alkalinity; this probably reflects equilibrium with atmospheric CO₂, with decreasing Ca (Fig. 18).

Ionic ratios and correlations

Figure 20 shows changes in certain ionic ratios with increased salinity of surface waters and groundwaters. These changes indicate distinct evolutionary processes in these waters. Thus the Mg/Ca ratio (Fig. 20a) increases more rapidly relative to TDS in lake waters than in lake-bed groundwaters. This might reflect several concurrent processes. The concentration of Mg by evaporation in the lake waters is enhanced by the reduction of Ca due to equilibrium with atmospheric CO₂, and dolomitisation of calcite in the aquifers reduces the Mg concentration and counteracts the effect of ion exchange, in which Ca is adsorbed preferentially to Mg. In lake waters the Ca/alkalinity ratio (Fig. 20b) initially increases, then decreases with increased salinity beyond 1000 mg/L TDS; in the lake-bed groundwaters, the ratio increases until 10 000 mg/L TDS, then decreases. The latter effect is due to mixing with lake waters that contribute alkalinity. The Ca/SO₄ ratio (Fig. 20c) increases in regional groundwaters until about 1000 mg/L TDS, then decreases. The initial increase reflects dissolution of aquifer matrix, releasing Ca; the subsequent decrease reflects the taking up of Ca in precipitation of carbonate minerals whereas SO₄ remains in solution. In surface waters the Ca/SO₄ ratio decreases throughout with increased salinity. Some Ca is taken up in precipitation, whereas SO₄ concentrations increase with evaporation.

The ionic ratios are different for lake-bed groundwaters at different depths. The deeper groundwaters continue regional groundwater trends, and the shallower groundwaters show the influence of mixing with lake waters.

Figure 21 shows the relationship between alkalinity (HCO₃ + CO₃) and total hardness (Ca + Mg). This ratio is close to unity for the fresher catchment groundwaters. In the more saline groundwaters the ratio is close to 0.5, indicating that precipitation of carbonate minerals takes place. In the fresher surface waters the alkalinity/hardness ratio is close to unity but with increased salinity it decreases as carbonate minerals precipitate.

Solution chemistry

Saturation indices are defined as the logarithms of the ion activity product divided by the equilibrium constant. In this study, the saturation indices and CO₂ partial pressures of the ionic components have been calculated using an unpublished BMR computer program 'ACTIVITY' written by J.S. Hanor, and based on Pitzer's equations (Pitzer, 1973) as developed by Harvie & Weare (1980) and Harvie & others (1984).

Figure 22 shows saturation indices for dolomite, calcite, and gypsum, plotted against salinity. Saturation for dolomite (SI_D = 0) is achieved at low salinities in catchment groundwaters and in creek waters (Fig. 22a). Saturation indices for dolomite increase in creek and

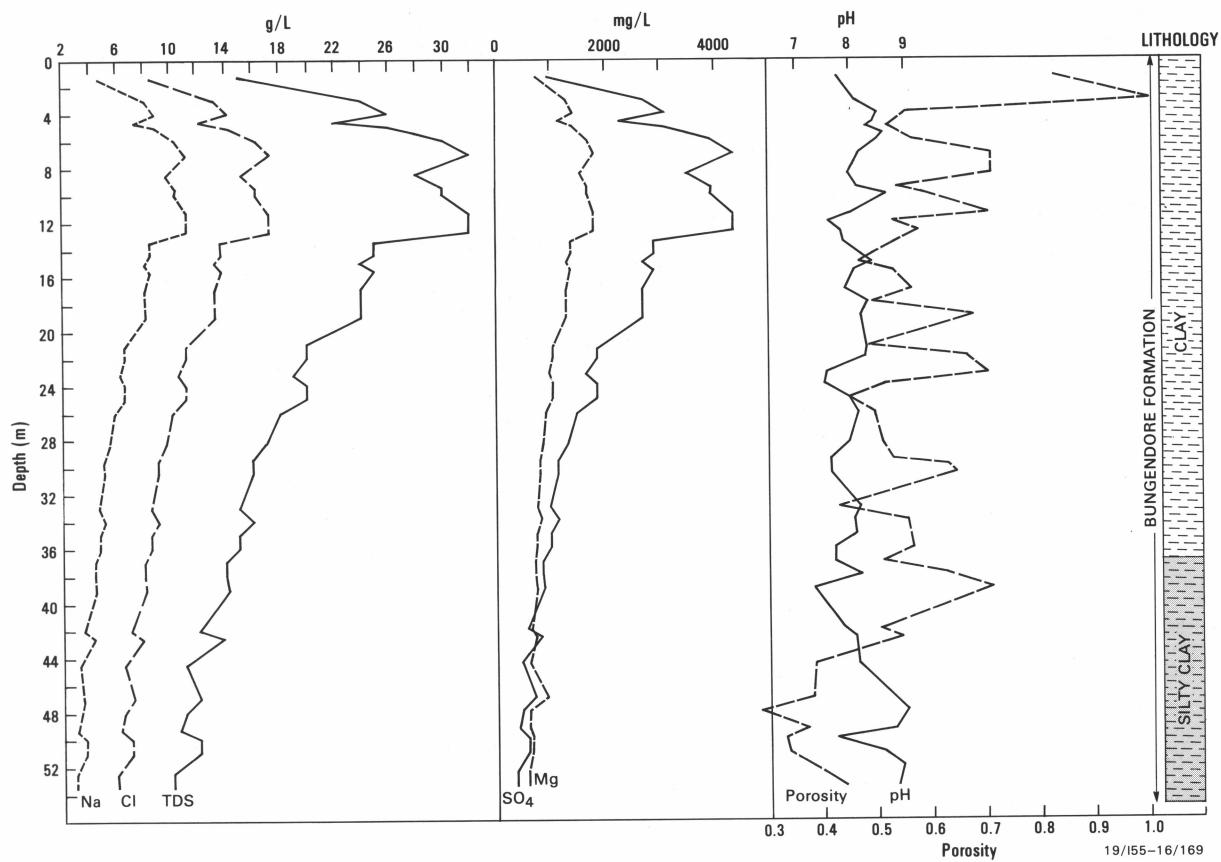


Figure 13. Pore-water chemistry and porosity, bore 352.

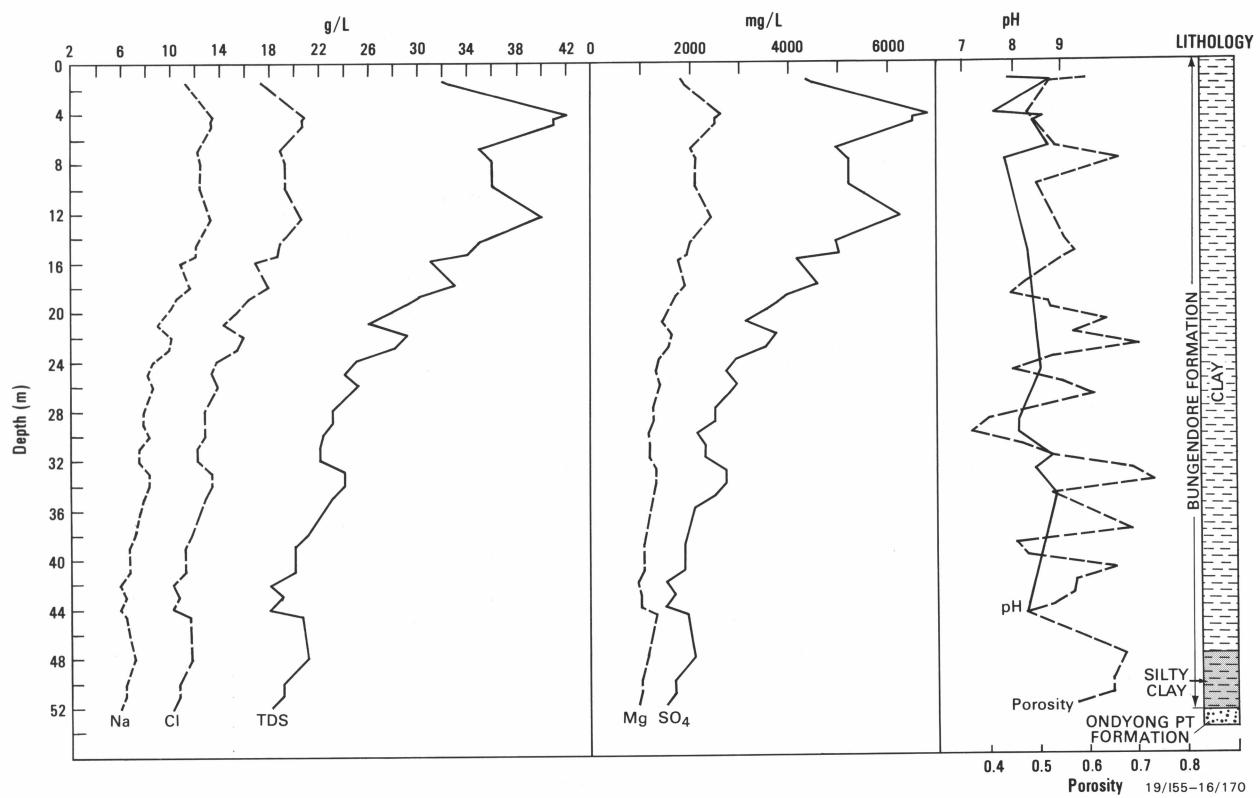


Figure 14. Pore-water chemistry and porosity, bore 354.

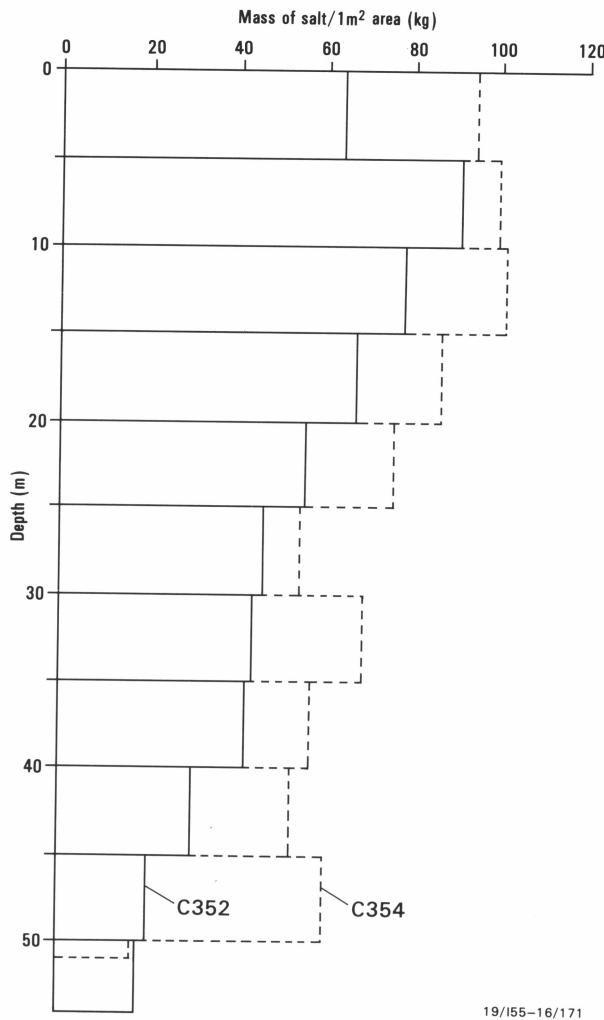


Figure 15. Salt accumulation in the aquitard beneath Lake George.

lake waters with increasing salinity. In the catchment groundwaters, saturation indices for dolomite also increase with increasing salinity. The saturation indices decrease then increase again in the saline groundwaters beneath the lake bed.

Similar trends are observed for saturation indices for calcite (Fig. 22b), except that brackish regional groundwaters are in equilibrium for calcite, i.e. $SI_C = 0$. The sample from 2 m below the lake bed has a low saturation index for both dolomite and calcite, compared with samples from 10 m depth and from lake waters. This is probably due to mixing between the lake waters and groundwaters. Two waters that are individually saturated for calcite at different P_{CO_2} partial pressures can mix to produce a solution that is undersaturated for calcite (Bögli, 1971). At Lake George, there is mixing of two waters at different P_{CO_2} : surface waters with high P_{CO_2} and groundwaters with less P_{CO_2} , both of which are saturated for calcite and dolomite. This produces a mixed water that is not, in fact, undersaturated, but is somewhat less saturated than the two initial waters.

Saturation indices for dolomite and calcite derived from aquitard pore waters tend to be grouped separately on

the diagrams (Fig. 22). They plot between the saline lake waters and equivalent aquifer waters, reflecting the dual influence of infiltrating lake water and upwards flow of groundwater.

Saturation indices for gypsum (Fig. 22c) show different trends for surface waters and groundwaters. With increasing salinity, saturation indices increase in surface waters up to a constant level at about 1000 mg/L TDS. Saturation indices for groundwaters increase with increasing salinity, and the most saline aquitard pore waters at 10 m below the lake bed are in equilibrium with gypsum. These are mixed waters and their saturation indices for gypsum are the average of two initial waters, i.e. the lake water and deeper groundwaters.

Figure 23 shows the relationship between saturation indices for dolomite and calcite and the calculated partial pressure of CO_2 for surface waters and groundwaters. For the surface waters, the plots of saturation indices show trends towards supersaturation with decreasing P_{CO_2} . As P_{CO_2} decreases towards its atmospheric value, $10^{-3.5}$, the trend line flattens. For the groundwaters there is a general trend towards supersaturation from catchment through lake-bed groundwaters, but a wide scatter of P_{CO_2} values. For lake-bed groundwaters, the degree of saturation for dolomite and calcite increases with increasing P_{CO_2} in bore 355, and with decreasing P_{CO_2} in bore 353. This relationship for lake-bed groundwaters is controlled by dissolution and precipitation reactions and mixing. The position of aquitard pore waters on these diagrams is closer to that of surface waters than of aquifer groundwaters.

Ion transfer

Ion transfer calculations trace the amount of substance (moles) gained as a result of dissolution, and lost as a result of precipitation of minerals and ion exchange, during the evolution of the lake waters and lake-bed groundwaters. These calculations are similar to those for evaporation budgets based on chloride concentration factors for continental brines (Eugster, 1970). In this study, ion transfer has been related to chloride concentration factors and compared with actual chemical analyses of Lake George groundwaters in the early phase of solute concentration (cf. Jankowski & Jacobson, 1990). Chloride is considered to be a conservative element up to the halite precipitation stage; halite only occurs as surface encrustation after long dry periods in Lake George. Tables 2 and 3 show ion transfer calculations for lake-bed groundwaters and lake waters in relation to the chloride concentration factors. For these calculations the inflow waters are taken as the freshest catchment groundwaters (Table 2) and creek waters (Table 3). The calculated gains from dissolution or losses from precipitation are plotted for individual ions against the concentration factor in Figures 24 and 25.

For lake-bed groundwaters (Fig. 24), alkalinity values decrease markedly relative to chloride as a result of precipitation of carbonate minerals. In the most saline groundwaters, the calculated loss is about 1450 mmol/L taken up in precipitation. Values of Ca, Mg, and Na decrease more slowly with calculated losses of 200, 350 and 250–350 mmol/L for these three ions. Ca and Mg are probably taken up in precipitation of carbonate minerals, and Na in ion exchange with clays. However, data from the two boreholes 353 and 355 show different

Table 1. Chemical analyses of surface waters and groundwaters.

Sample	Depth	Lake stage	TDS mg/L	Na mg/L	K mg/L	Ca mg/L	Mg mg/L	HCO ₃ mg/L	CO ₃ mg/L	SO ₄ mg/L	Cl mg/L	pH	Chemical types ¹
Creek waters													
Allianoy Cr	—	1.16	100	6	6	2	2	20	0	1	7	6.1	HCO ₃ -Cl-Na-Mg
Butmaroo Cr	—	1.16	190	42	1	15	19	117	0	10	65	7.6	HCO ₃ -Cl-Na-Mg
Butmaroo Cr	—	3.17	205	37	2	14	15	101	0	43	40	7.4	HCO ₃ -Cl-SO ₄ -Na-Mg-Ca
Collector Cr	—	4.14	217	40	0	14	11	29	0	77	50	6.9	SO ₄ -Cl-Na-Mg-Ca
Taylors Cr	—	1.16	310	62	2	15	26	68	0	10	148	7.3	Cl-HCO ₃ -Na-Mg
Butmaroo Cr	—	4.12	405	49	3	38	35	276	0	3	112	7.3	HCO ₃ -Cl-Mg-Na-Ca
Collector Cr	—	3.76	406	57	1	38	39	148	0	33	157	7.5	Cl-HCO ₃ -Mg-Na-Ca
Turralo Cr	—	4.12	640	116	3	52	53	287	0	43	225	7.4	Cl-HCO ₃ -Na-Mg-Ca
Collector Cr	—	1.16	645	80	1	70	73	268	0	61	238	8.0	Cl-HCO ₃ -Mg-Ca-Na
Collector Cr	—	1.77	1190	101	2	86	122	244	0	111	440	8.0	Cl-HCO ₃ -Mg-Na-Ca
Catchment bores — groundwaters													
Bore 47702	76.0	1.61	156	34	1	13	9	135	0	15	18	6.8	HCO ₃ -Na-Mg-Ca
Bore 30823	35.0	1.69	203	45	1	13	16	134	0	11	51	7.3	HCO ₃ -Cl-Na-Mg
Bore LG4B	39.5	3.00	207	36	1	17	17	115	0	5	70	7.4	Cl-HCO ₃ -Na-Mg-Ca
Bore 30844	65.0	1.61	217	40	0	17	23	199	0	11	27	8.0	HCO ₃ -Mg-Na
Bore 30839	50.0	1.71	225	39	1	20	23	195	0	11	35	7.9	HCO ₃ -Cl-Mg-Na-Ca
Bore 30829	62.0	1.69	245	48	1	19	14	189	0	46	24	7.8	HCO ₃ -SO ₄ -Na-Mg-Ca
Collector Hotel	40.0	4.14	250	43	0	20	19	138	0	10	65	6.8	HCO ₃ -Cl-Na-Mg-Ca
Bore 30707	22.0	3.06	252	45	3	21	17	73	0	34	97	6.6	Cl-HCO ₃ - Na-Mg-Ca
Bore 50047	64.0	2.41	279	51	2	10	34	173	0	10	87	7.2	HCO ₃ -Cl-Mg-Na
Bore 30844	65.0	1.05	283	54	1	12	26	250	0	17	40	7.3	HCO ₃ -Cl-Na-Mg-Ca
Bore 30708	28.0	3.06	298	71	3	19	17	134	0	26	99	6.9	Cl-HCO ₃ -Na-Mg
Bore 30706	30.0	3.06	314	66	2	24	22	131	0	22	113	7.7	Cl-HCO ₃ -Na-Mg-Ca
Bore 30844	65.0	2.35	338	54	5	50	17	582	0	14	113	7.9	HCO ₃ -Cl-Na-Ca-Mg
Bore LG7	40.0	3.00	380	83	7	24	27	195	0	40	105	8.2	HCO ₃ -Cl-Na-Mg
Bore 30835	57.0	1.69	421	89	1	35	35	343	0	13	80	8.4	HCO ₃ -Cl-Na-Mg-Ca
Bore 30809	56.0	1.51	531	134	3	22	36	211	0	31	201	8.0	Cl-HCO ₃ -Na-Mg
Collector	40.0	1.47	610	122	1	41	46	115	0	22	319	8.2	Cl-Na-Mg
Bore 30844	65.0	1.61	658	137	2	49	50	433	0	41	166	8.1	HCO ₃ -Cl-Na-Mg
Bore LG 9	39.5	3.00	695	106	1	58	60	283	0	23	265	6.7	Cl-HCO ₃ -Mg-Na-Ca
Bore LG 18	38.0	3.00	822	83	1	58	60	256	0	14	250	6.5	Cl-HCO ₃ -Mg-Na-Ca
Bore 42933	43.0	2.76	824	83	2	58	61	239	0	31	250	6.6	Cl-HCO ₃ -Mg-Na-Ca
Bore LG4C	39.5	3.00	824	134	1	75	82	335	0	25	365	7.3	Cl-HCO ₃ -Mg-Na-Ca
Bore 42686	40.0	1.51	848	146	2	51	93	250	0	28	406	8.1	Cl-HCO ₃ -Mg-Na
Bore 42686	40.0	2.36	906	153	2	81	76	342	0	31	395	7.2	Cl-HCO ₃ -Na-Mg-Ca
Bore 30705	23.0	3.06	955	283	3	33	43	400	0	58	339	7.7	Cl-HCO ₃ -Na-Mg-Ca
Bore 42685	57.0	2.71	993	181	2	84	84	283	0	23	265	6.9	Cl-HCO ₃ -Na-Mg-Ca
Bore LG 14	56.5	3.00	993	181	2	83	84	354	0	36	432	6.9	Cl-HCO ₃ -Na-Mg-Ca
Bore LG 16	39.5	3.00	1220	138	2	97	73	366	0	20	375	6.7	Cl-HCO ₃ -Na-Mg-Ca
Bore 48089	44.0	3.08	1354	188	3	100	80	364	0	17	490	6.9	Cl-HCO ₃ -Na-Mg-Ca
Bore LG 17	56.5	3.00	1526	190	2	94	85	359	0	12	505	7.0	Cl-HCO ₃ -Na-Mg-Ca
Bore 42932	57.0	2.76	1556	190	2	94	84	395	0	19	505	7.0	Cl-HCO ₃ -Na-Mg-Ca
Bore 42934	47.0	2.73	1956	250	2	119	105	383	0	25	715	6.9	Cl-HCO ₃ -Na-Mg-Ca
Bore LG 19	45.5	3.00	2060	250	2	119	107	388	0	26	715	6.8	Cl-HCO ₃ -Na-Mg-Ca
Lake bed aquifers — groundwaters													
Bore 351	1	—	34766	11800	33	160	1100	726	0	3100	18210	7.4	Cl-Na
Bore 353	10	—	40602	13000	15	330	1570	732	0	4750	20570	7.3	Cl-Na
	10	—	40680	13000	0	280	1400	760	0	4900	20720	7.5	Cl-Na
	50	—	14640	4220	7	420	640	547	0	730	8350	7.4	Cl-Na-Mg
	100	—	9391	2640	4	390	400	240	0	285	5552	6.8	Cl-Na
Bore 355	10	—	45877	13550	29	465	2180	1273	0	10200	18816	7.3	Cl-SO ₄ -Na-Mg
	10	—	46511	14400	18	500	1825	832	0	8180	21172	7.5	Cl-SO ₄ -Na
	10	—	46995	14300	17	485	1820	859	0	8300	21643	7.3	Cl-SO ₄ -Na
	10	—	47038	13700	7	410	1930	1284	0	11200	19140	7.4	Cl-SO ₄ -Na-Mg
	10	—	48354	14000	19	540	2020	1014	0	11600	19619	7.7	Cl-SO ₄ -Na-Mg
	50	—	27596	8400	0	540	1000	511	0	2420	14980	7.5	Cl-Na
	50	—	28495	8380	9	600	1170	533	0	2880	15060	7.5	Cl-Na
	50	—	29329	8720	8	610	1230	521	0	3060	15431	7.8	Cl-Na
	50	—	30261	8700	5	660	1300	509	0	2720	16621	7.2	Cl-Na
	100	—	12147	3870	5	245	406	302	0	630	6840	7.5	Cl-Na
Lake bed aquitard — porewaters													
Bore 352	9.7	—	30220	8970	46	320	1280	760	0	4970	13880	8.16	Cl-SO ₄ -Na-Mg
	15	—	25850	7370	47	400	1270	530	0	2970	13260	8.42	Cl-Na-Mg
	30	—	17900	5585	50	375	785	153	0	1040	9940	8.38	Cl-Na
	47	—	12800	3430	30	465	890	82	0	690	7180	7.60	Cl-Na-Mg
Bore 354	15.5	—	38800	12030	42	509	1930	765	0	5000	18560	8.30	Cl-Na- Mg
	30	—	25300	8180	38	465	1140	389	0	2090	12660	8.10	Cl-Na
	44.6	—	21950	6340	29	600	1310	328	0	1890	11460	8.25	Cl-Na-Mg
Lake waters													
Gearys Gap	—	4.05	1350	433	5	23	25	220	0	79	615	8.1	Cl- Na
Kennys Point	—	3.17	1627	553	5	9	36	251	0	92	781	8.0	Cl- Na
Kennys Point	—	3.17	1730	585	6	22	38	263	0	97	830	7.8	Cl- Na
Gearys Gap	—	2.69	2018	670	6	53	42	279	11	114	977	8.5	Cl- Na
Lake George	—	1.16	2415	840	7	29	49	311	0	148	1176	8.0	Cl- Na
Gearys Gap	—	1.74	5640	1960	9	32	126	650	50	315	2775	8.7	Cl- Na
Kennys Point	—	1.46	7163	2504	13	22	152	930	33	325	3535	8.9	Cl- Na
Rocky Point	—	1.00	7810	2650	30	50	160	703	38	450	4050	8.7	Cl- Na
Lake George	—	1.18	9540	3350	17	31	202	845	75	545	4800	8.8	Cl- Na
Gearys Gap	—	1.46	9893	3506	17	18	205	1085	66	470	4995	8.9	Cl- Na
Lake George	—	0.30	12817	4850	26	101	200	1712	0	1480	5740	7.8	Cl- Na
Rocky Point	—	0.59	28831	10500	23	24	585	551	381	1660	15386	9.3	Cl-Na
Kennys Point	—	0.83	38900	13700	40	35	740	1515	450	2391	20160	8.9	Cl-Na
Rocky Point	—	0.60	42081	14950	34	25	1000	812	361	2700	22603	9.0	Cl-Na
Gearys Gap	—	0.83	44800	15900	47	35	860	1565	595	2823	23005	8.9	Cl-Na

¹Classification after Szczukariew & Priklonski (Alekin, 1970)

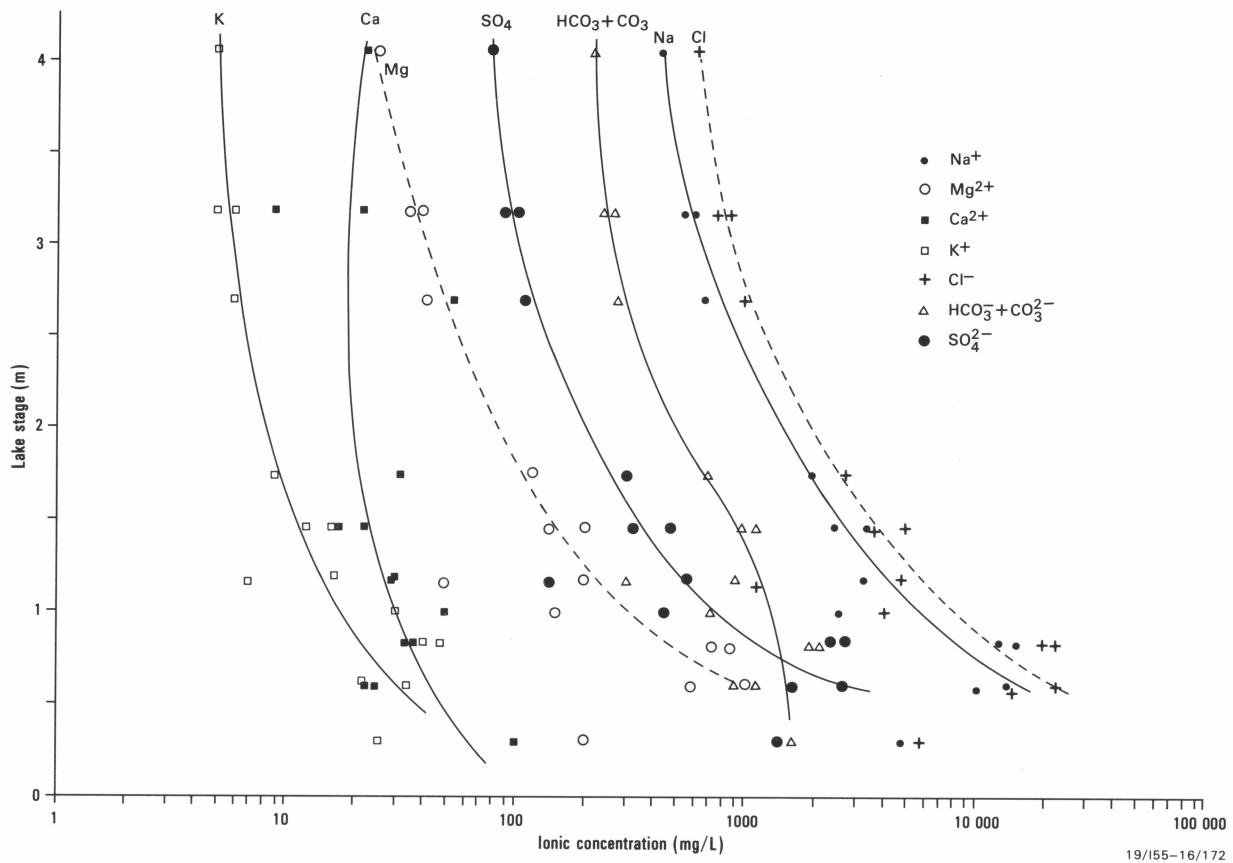


Figure 16. Compositional changes of major ions with varying lake stage and salinity.

values for losses of Mg and Na. Low values for losses of K are possibly due to this ion being partly taken up in ion exchange for clays. Apparent excessive losses of alkalinity compared with the cations are because its derivation is partly atmospheric. The SO_4^{2-} ion shows losses of 25 mmol/L in bore 355, but gains of 50 mmol/L in bore 353. These slight differences reflect the closeness to equilibrium with gypsum.

In the lake waters (Fig. 25), all ions are lost relative to chloride. Alkalinity is taken up in the precipitation of carbonate minerals, and the calculated loss is up to 800 mmol/L. When compared with the equivalent value for the groundwaters, this suggests that alkalinity is renewed by rainwater. The Ca and Mg values decrease as a result of precipitation of carbonate minerals; calculated losses are 180 and 200 mmol/L respectively. The losses of Na, K and SO_4^{2-} are up to 100 mmol/L. Na and K are possibly taken up in ion exchange with clays. The reason for SO_4^{2-} losses is not clear, as according to thermodynamic calculations, gypsum is not precipitated.

Stable isotope chemistry

Lake George groundwater samples were analysed for oxygen-18 and deuterium, the stable isotopes of water (Table 4).

The amounts of D and ^{18}O in Canberra rainfall (40 km from Lake George) vary; $\delta^{18}\text{O}$ and δD values range from -2.27 to -13.02 ‰ and from -7.6 to -94.1 ‰ respectively (C.J. Barnes, CSIRO Division of Water Resources, personal communication, 1989). The $\delta^{18}\text{O} - \delta\text{D}$ relationship for Canberra rainfall is shown in

Figure 26. The stable isotope data plot on a line, the Local Meteoric Water Line:

$$\delta\text{D} = 8.52 \delta^{18}\text{O} + 15.23$$

This line is close to the World Meteoric Water Line (Craig, 1961) but has a slightly greater slope and higher intercept. The greater slope probably indicates rapid evaporation of fresh water from light rainfall (Dansgaard, 1964). The higher intercept probably reflects some modification of continental air masses over the Eastern Highlands by interaction of humid air from the Pacific Ocean (cf. Gat & Carmi, 1970).

The isotopic contents of Lake George groundwaters range from $+0.05\text{ ‰}$ at 2 m depth to -5.48 ‰ at 100 m depth for $\delta^{18}\text{O}$ and from -0.4 ‰ at 2 m depth to -32.9 ‰ at 100 m depth for δD . All samples are enriched in ^{18}O and plot to the right of the Local Meteoric Water Line for Canberra. This suggests that these groundwaters have been affected by evaporation during or since recharge. The regression relationships between δD and $\delta^{18}\text{O}$ for groundwater samples at various depths are given in Figure 26. Although the regression lines are based on a limited number of samples, the low slope for samples from 50 and 100 m (3.0 and 4.3 respectively) implies that a high degree of evaporation has taken place in the time since recharge. These slopes are typical of evaporation into relatively dry air (cf. Gat, 1971), suggesting that recharge of these waters took place under semi-arid conditions. For 10 m deep samples, the slope is 7.3, suggesting that these waters are affected by surface evaporation (Fontes & Gonfiantini, 1967).

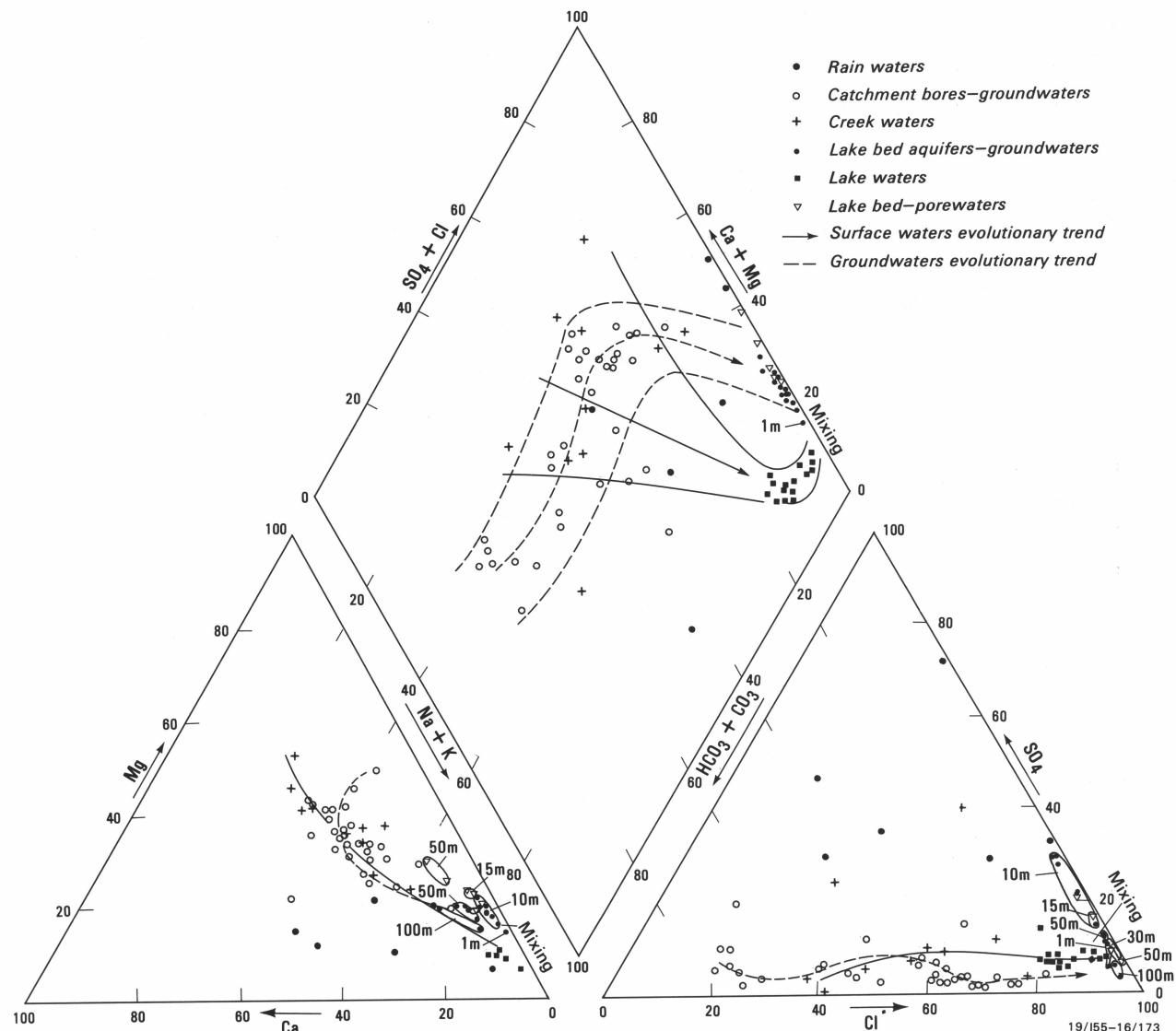


Figure 17. Trilinear diagram showing major ion hydrochemistry.

The deuterium-excess value has been calculated for groundwater samples from different depths. The deuterium-excess value, d , is given by Dansgaard (1964):

$$d = \delta D - 8 \delta^{18}\text{O}$$

For samples at 2 m and 10 m, low values of deuterium-excess have been derived, averaging -0.8 and $+0.8$ respectively. Low values of deuterium-excess are elsewhere associated with extensive evaporation before infiltration (Rozanski, 1985), and this is probably the case for the shallow groundwater at Lake George. For samples from 50 m and 100 m, the average values of deuterium-excess are 2 and 9 respectively. These values indicate that relatively little evaporation occurred during the recharge process. A linear relationship between samples from 2 and 10 m suggests some mixing of evaporated surface waters and groundwaters (cf. Frape & Fritz, 1982).

Tritium and chlorine-36 determinations

Selected Lake George groundwater samples were analysed for the radioisotopes tritium and chlorine-36. Results are shown in Table 4. Significant activity of tritium (3 T.U.) was observed in groundwater at 2 m below the lake-bed, indicating that the water is probably modern (cf. Calf, 1988). A sample from a depth of 10 m contained 0.3 T.U., suggesting an age of 25–50 years. Two other samples with little or no tritium are considered more than 50 years old.

Chlorine-36 is a naturally occurring radioactive isotope with a half-life of about 301 000 years. The high solubility of the chloride ion in water makes it a useful isotope for the study of the origin and age of groundwaters. Recent Australian studies of groundwater using chlorine-36 include those of Bentley & others (1986) in the Great Artesian Basin and Davie & others (1989) in the Murray Basin. These studies indicate that processes which can affect the chlorine-36 signal include radioactive decay, subsurface production, dissolution of ancient salt evaporites, evaporation and ion filtration,

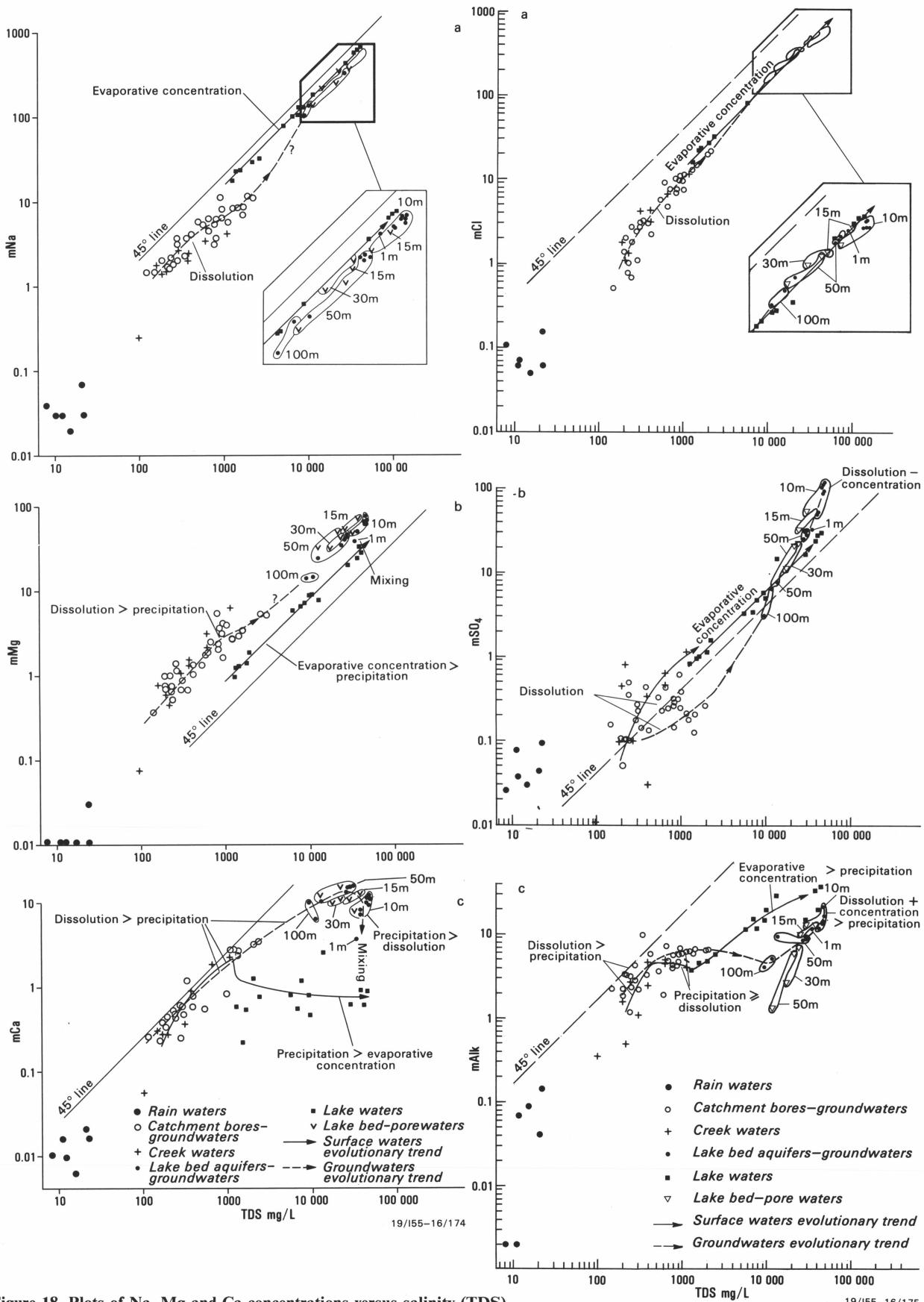
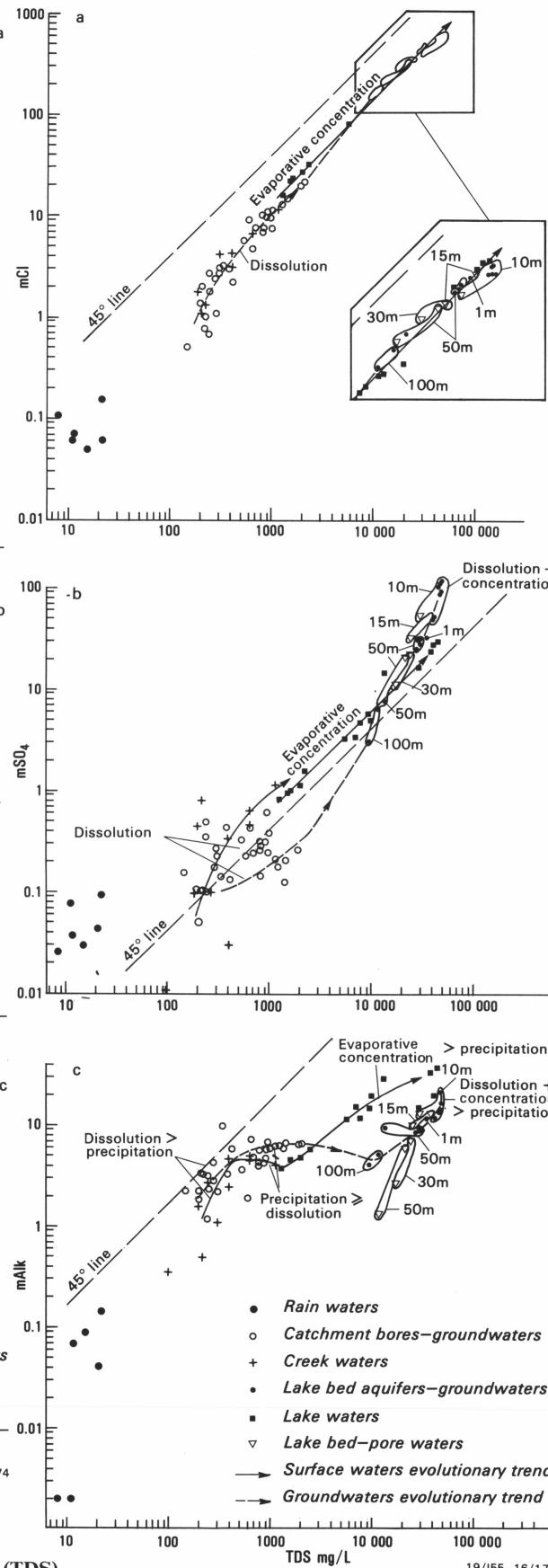


Figure 18. Plots of Na, Mg and Ca concentrations versus salinity (TDS).

mixing of two water bodies, and the addition of modern salt from atmospheric precipitation.

Figure 19. Plots of Cl, SO₄ and alkalinity concentrations versus salinity (TDS).



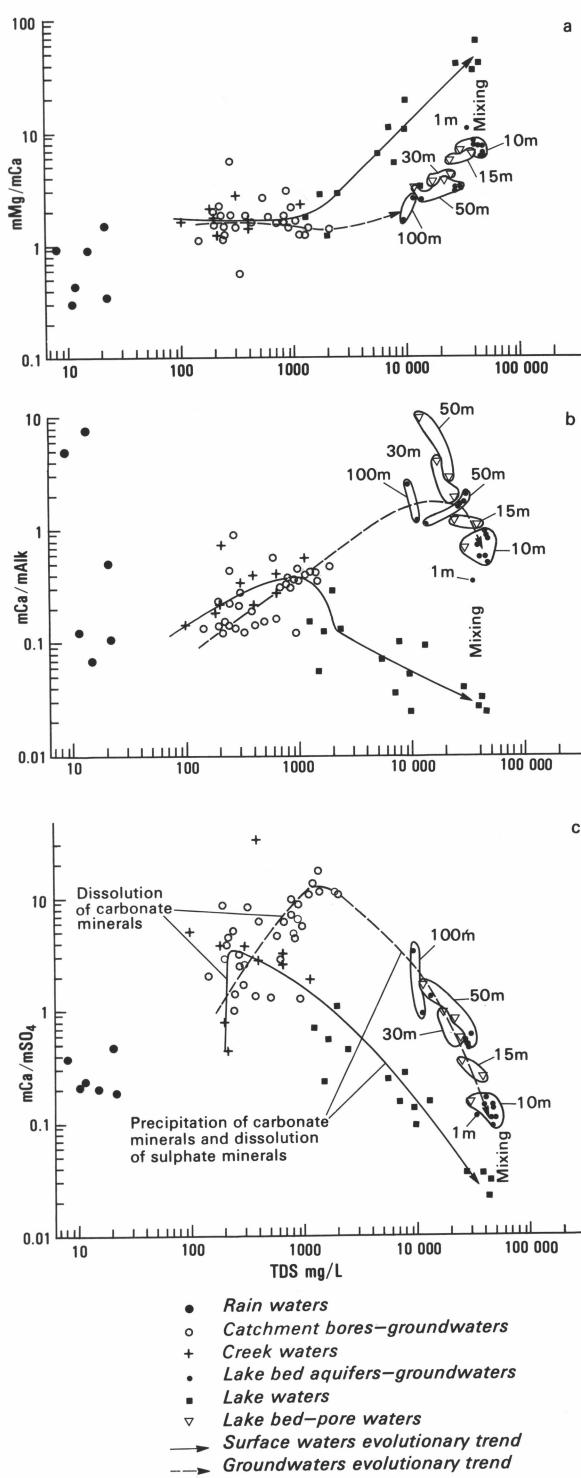


Figure 20. Plots of the ionic ratios Mg/Ca, Ca/Alkalinity and Ca/SO₄ versus salinity (TDS).

Six samples of Lake George groundwaters were analysed for chlorine-36, from two bores at 10, 50 and 100 m. A plot of $^{36}\text{Cl}/\text{Cl}$ versus $^{36}\text{Cl}/\text{L}$ is shown in Figure 27. For bore 353, displacement of the point to the left from 10 to 50 m suggests the addition of low salinity waters, containing very little ^{36}Cl (cf. Phillips & others, 1983). From 50 to 100 m, the displacement to the left and

downwards suggests decay of ^{36}Cl . For bore 355 from 10 m to 100 m, displacement of the point to the left suggests the addition of low salinity waters. There are evidently some differences in age between samples at 100 m in the two boreholes, and this may result from leakage of low salinity groundwaters from fractured rock aquifers at the lake margin into bore 355.

Figure 28 shows the relationship between ^{36}Cl and Cl concentrations in the groundwater. These contents are affected differently by various environmental processes, and this can be demonstrated with reference to a line from the origin of the plot. On this plot, relatively high concentrations of both ^{36}Cl and Cl are observed at 10 m depth where modern lake waters infiltrate. The linear relationship of the concentrations from 10 m to 100 m suggests that the dominant process is dilution.

Owing to the mixing of the waters in this system, it is not possible to derive rigorous ^{36}Cl ages from this data. The input value of the $^{36}\text{Cl}/\text{Cl}$ ratio is about 130×10^{-15} as suggested by the determined values for Lake George samples at 10 and 50 m. The standard radiometric decay equation (Bentley & others, 1986) suggests that the deeper groundwaters at 100 m are probably several tens of thousands of years old. The sample at 100 m in bore 355 is possibly more than 100 000 years old.

Discussion: hydrological processes

Hydrological processes in the Lake George basin are illustrated in Figure 29. In wet lake-full periods (Fig. 29a), salt enters the lake from creeks draining the catchment. Dilute surface water infiltrates the lake bed and balances the upwards movement of groundwater. A zone of hydrostatic balance between surface water and groundwater is evident at about 10 m below the lake bed. During drying-out phases (Fig. 29b) the lake water becomes saline through evaporation. In dry periods, conditions are playa-like; capillary-zone evaporation concentrates salt and generates saline waters in the 10 m zone below the lake bed. Salt diffuses downwards through the aquitard despite the upwards movement of groundwater. Thus salt accumulates in the wet periods and is concentrated in the dry periods, and there is some dilution in the wet periods. The low overall accumulation rate suggests that there is some recycling of salt between the surface water and groundwater systems, and some loss of efflorescent salt from the lake bed by wind action. The mechanisms for recycling may be diffusional transfer of dissolved ions from saline lake-bed porewaters to more dilute lake waters during refilling phases (cf. Lerman & Brunskill, 1971), and the transfer of ions from saline lake waters to shallow groundwaters during drying phases (cf. Lerman & Jones, 1973).

These cyclical processes might have been operating within the basin for 2×10^6 years, i.e. during the last stages of lacustrine sedimentation. The double peak of the salinity profile may indicate two periods of maximum aridity. The displacement of the salinity profile downwards may have occurred between 27 000 and 21 000 years B.P., when the 37 m deep lake overflowed through Gearys Gap (Coventry, 1976). Authigenic gypsum and halite (indicating arid periods) in the sequence of generally freshwater, lacustrine and fluvial

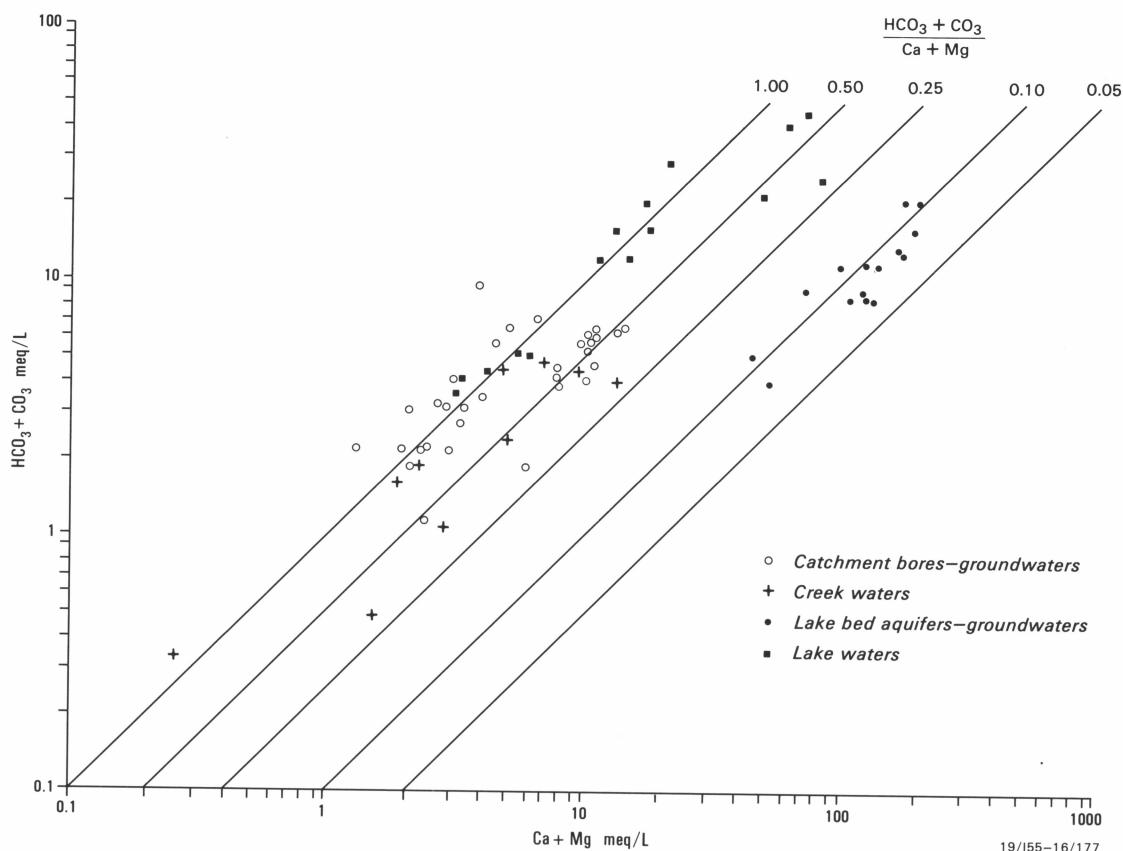


Figure 21. Plot of alkalinity ($\text{HCO}_3 + \text{CO}_3$) versus hardness ($\text{Ca} + \text{Mg}$).

sediments indicate older and larger climatic and hydrological fluctuations. Several different processes have contributed to the present day hydrochemistry of Lake George surface waters and groundwaters. The most important is mixing between lake waters and groundwaters in a zone of up to 15 m below the lake bed. The creek and lake waters evolve by evaporative concentration, dissolution and mineral precipitation. The regional and deeper lake-bed groundwaters evolve by dissolution and mineral precipitation in the flow system.

Figure 30 shows possible pathways of chemical evolution of Lake George waters. The fresher lake waters, up to 3000 mg/L TDS, are Cl-Na rich, and this suggests dissolution of halite crusts after dry periods. With increasing salinity, mainly because of evaporation, concentrations of all ions increase but their proportions change. The molar alkalinity concentration is greater than the molar Ca concentration throughout the change in salinity, although the ratio of molar alkalinity to molar Mg changes (Fig. 30). The ionic sequence for lake-waters up to about 10 000 mg/L TDS is $\text{Na} > \text{Mg} > \text{Ca} > \text{K}$ and $\text{Cl} > \text{HCO}_3 + \text{CO}_3 > \text{SO}_4$. In more saline lake waters the sequence becomes $\text{Na} > \text{Mg} > \text{Ca} > \text{K}$ and $\text{Cl} > \text{SO}_4 > \text{HCO}_3 + \text{CO}_3$. These changes are caused by evaporative concentration coinciding with precipitation of carbonate minerals which takes up alkalinity. The alkalinity concentration actually increases because of renewal by rainwater in lake-full conditions.

The chemistry of the shallow lake-bed groundwaters is affected mainly by mixing with lake waters, and dissolution and precipitation reactions. Deeper lake-bed and

catchment groundwaters evolve through dissolution and precipitation of minerals, mainly carbonate, in the groundwater flow system. All groundwaters beneath the lake bed have the same ionic sequence, $\text{Na} > \text{Mg} > \text{Ca} > \text{K}$ and $\text{Cl} > \text{SO}_4 > \text{HCO}_3$. In these waters molar alkalinity is close to equilibrium with molar Ca. In the shallower groundwaters, the molar SO_4 concentration is greater than molar Mg, and in the deeper groundwaters molar Mg is greater than molar SO_4 . Thus Lake George waters can be considered in terms of four hydrochemical types, evolving through changing molar ratios of Mg, SO_4 , Ca and alkalinity (Fig. 30).

The evolutionary pathway for surface waters is simpler than that for groundwaters, reflecting mainly the evaporation of surface waters and their infiltration as Cl-Na waters. The pathway for groundwaters reflects the more complex processes pertaining to the groundwater system, especially the effects of interaction with the aquifer matrix.

Conclusions

1. The hydrological regime of Lake George is one of cyclical wet and dry conditions. Salt is transported into the lake from the catchment in wet periods. The lake salinity is inverse to water volume. In dry periods the lake acts as a playa, with capillary-zone evaporation.
2. Sand aquifers beneath the lake bed have upwards pressures directed through a clay aquitard. There is hydrostatic balance at a depth of 10–12 m beneath

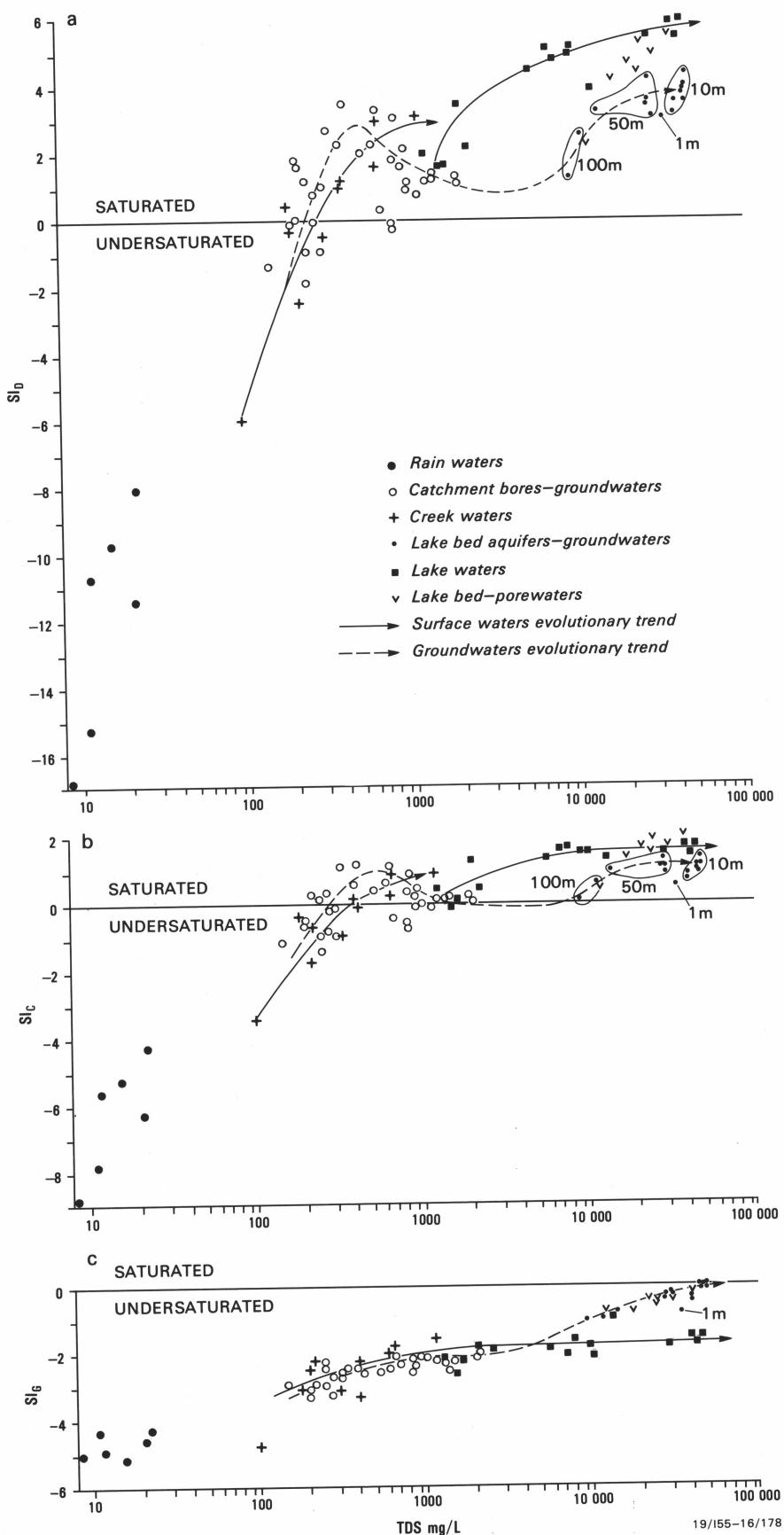


Figure 22. Saturation indices for dolomite, calcite and gypsum, as a function of salinity.

Table 2. Ion transfer calculations for Lake George, lake-bed groundwaters.

Sample	C.F. ¹	Cl mmol/L	Na mmol/L	K mmol/L	Ca mmol/L	Mg mmol/L	Alkalinity mmol/L	SO ₄ mmol/L
Inflow waters	1	1.22	1.93	0.03	0.42	0.85	2.90	0.17
34766	421.02	0	-299.30	-11.79	-172.84	-312.61	-1209.06	-39.30
40602	475.57	0	-352.38	-13.89	-191.51	-339.63	-1367.15	-31.40
40680	479.05	0	-359.10	-14.30	-194.21	-349.59	-1376.79	-30.43
14640	193.05	0	-189.03	-5.61	-70.60	-137.76	-550.89	-25.22
9391	128.36	0	-132.90	-3.75	-44.18	-92.65	-368.31	-18.85
45877	435.02	0	-250.20	-12.31	-171.11	-280.08	-1240.70	+32.24
46511	489.49	0	-318.35	-14.22	-193.11	-340.98	-1405.88	+1.95
46995	500.39	0	-343.73	-14.58	-198.06	-350.45	-1437.05	+1.34
47038	442.52	0	-258.44	-13.10	-175.63	-269.73	-1262.27	+41.37
48354	453.59	0	-266.46	-13.12	-177.04	-302.44	-1298.79	+43.65
27596	346.34	0	-303.06	-10.38	-131.99	-253.25	-996.02	-33.69
28495	348.19	0	-307.50	-10.22	-131.27	-247.82	-1001.01	-29.21
29329	356.76	0	-309.25	-10.50	-134.62	-252.64	-1026.06	-28.79
30261	384.28	0	-363.23	-11.40	-144.93	-273.15	-1106.07	-37.01
12147	158.14	0	-136.87	-4.61	-60.31	-117.72	-453.66	-20.32

¹ Concentration factor, based on chloride
Positive value indicates gain of ions
Negative value indicates loss of ions

the lake bed and this coincides with maximum groundwater salinity.

3. A nearly linear salinity profile in the aquitard suggests that salt has diffused downwards over a long period of time. The salinity profile has been displaced downwards by the superimposition of fresh water.
4. Major-ion hydrochemistry indicates that the lake waters evolve by evaporative concentration and precipitation of carbonate minerals. Regional groundwaters evolve by dissolution, and there is mixing with infiltrating lake waters in the 10–12 m beneath the lake bed.
5. All waters in the catchment are saturated for dolomite and calcite, but undersaturated for gypsum. The mixing of lake waters with groundwater is reflected in a lesser degree of saturation.
6. Ion transfer calculations demonstrate substantial loss of HCO₃ from both lake waters and groundwater as a result of mineral precipitation. Losses of Mg, Ca, Na and K are also evident. Sulphate is lost in lake waters but gained in parts of the groundwater system through dissolution.
7. Stable isotope and tritium data confirm the effect of mixing lake waters with groundwaters in the top 12 m.

8. Chlorine-36 determinations suggest that groundwater 100 m beneath the lake bed is tens of thousands of years old.

9. Lake George is a natural analogue for a wastewater disposal basin with a thick clay aquitard; its net salt accumulation has occurred over a period of 1–2 million years.

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We thank Jeff Hanor (Louisiana State University) and Ray Evans (BMR) for access to unpublished work on the Geera Clay, Keith Fifield and Raoul Davie (Australian National University) for chlorine-36 determinations of groundwater samples, Jon Olley (CSIRO Division of Water Resources) for stable isotope determinations, and Chris Barnes (CSIRO Division of Water Resources) for unpublished data on the stable isotope composition of Canberra rainfall. Graeme Calf (Australian Nuclear Science and Technology Organisation) undertook tritium determinations. The New South Wales Department of Water Resources provided water bore data for the Lake George catchment. BMR staff who provided technical assistance included Andre Zoska, Bill Keeley, Knut Reine and Greg Sparksman. We thank Ray Evans and two anonymous referees for comments on the manuscript.

Table 3. Ion transfer calculations for Lake George, lake waters.

Sample	C.F. ¹	Cl mmol/L	Na mmol/L	K mmol/L	Ca mmol/L	Mg mmol/L	Alkalinity mmol/L	SO ₄ mmol/L
Inflow waters	1	1.05	1.23	0.08	0.30	0.43	1.30	0.19
1350	16.47	0	-1.47	-1.14	-4.36	-5.97	-17.81	-2.26
1627	20.92	0	-1.73	-1.48	-6.04	-7.41	-23.09	-2.96
1730	22.23	0	-1.95	-1.55	-6.11	-7.89	-24.60	-3.16
2018	26.17	0	-3.11	-1.85	-6.51	-9.40	-29.27	-3.72
2415	31.50	0	-2.28	-2.24	-8.71	-11.38	-35.86	-4.36
5640	74.33	0	-6.35	-5.47	-21.46	-26.42	-85.17	-10.65
7163	94.69	0	-7.78	-6.93	-27.80	-34.00	-107.33	-14.36
7810	108.48	0	-18.43	-7.56	-31.23	-39.54	-128.90	-15.64
9540	128.57	0	-12.74	-9.43	-37.72	-46.35	-152.09	-18.42
9893	133.80	0	-12.39	-9.83	-39.61	-48.45	-155.09	-20.18
12817	153.75	0	-21.48	-11.13	-43.51	-57.14	-171.85	-13.40
28831	412.13	0	-51.19	-31.03	-122.79	-151.14	-520.57	-59.95
38900	540.01	0	-69.59	-40.41	-160.80	-199.13	-669.90	-76.30
42081	605.44	0	-95.87	-45.59	-180.65	-216.25	-767.96	-85.34
44800	616.21	0	-67.82	-46.08	-183.62	-226.59	-765.78	-86.08

¹ Concentration factor, based on chloride
Negative value indicates loss of ions

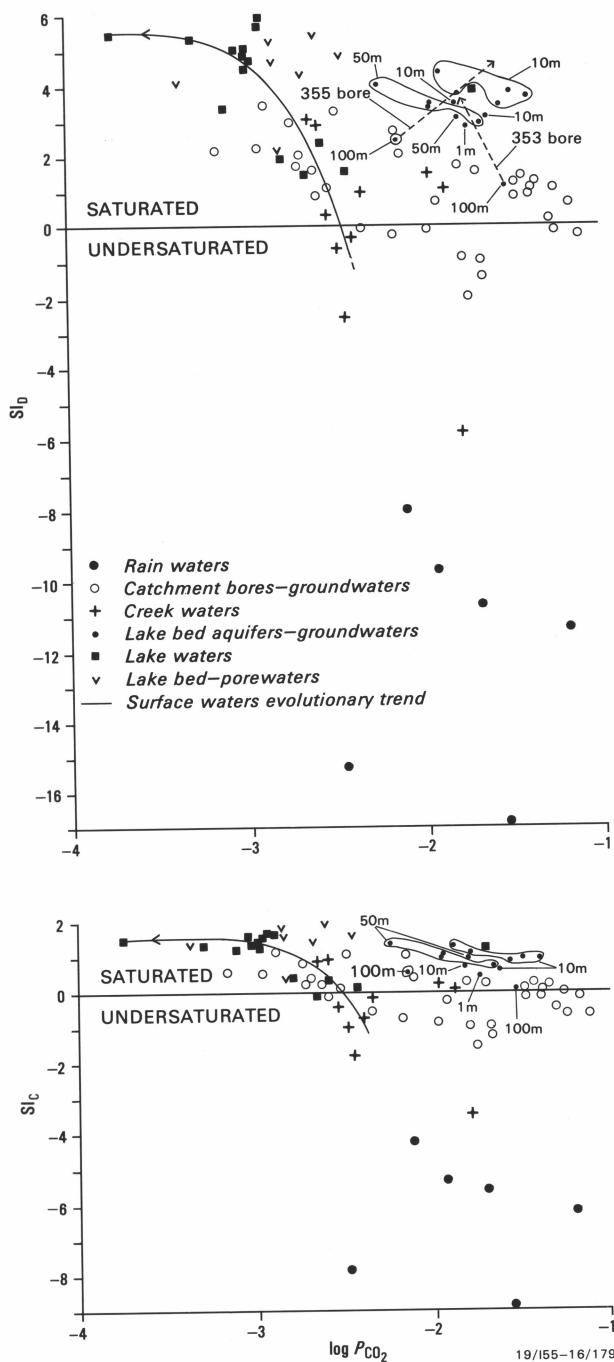


Figure 23. Relationship between partial pressures of CO_2 and saturation indices.

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Table 4. Isotope data for Lake George groundwaters.

Location	Depth (m)	D (‰ SMOW)	^{18}O (‰ SMOW)	^{36}Cl ($^{36}\text{Cl}/\text{Cl} \times 10^{-15}$ ‰)	^3H (T.U.)
355	10	-26.3	-3.32	124(± 9%)	0.3±0.3
355	10	-27.4	-3.69		
355	50	-16.8	-2.33	132(± 17%)	0.0±0.3
355	50	-14.6	-1.98		
355	100	-32.9	-5.48	113(± 11%)	0.1±0.3
353	10	-13.2	-1.70	122(± 12%)	
353	10	-15.2	-1.88		
353	50	-16.6	-2.44	121(± 7%)	
353	100	-28.7	-4.51	80(± 8%)	3.0±0.4
351	2	-0.4	+0.05		
352 ¹	15	-14.79	-2.52		
352 ¹	30	-13.01	-1.51		
352 ¹	47	-16.83	-2.67		
354 ¹	15.5	-13.80	-1.55		
354 ¹	30	-11.75	-0.59		
354 ¹	44.6	-15.94	-2.13		

¹Pore waters

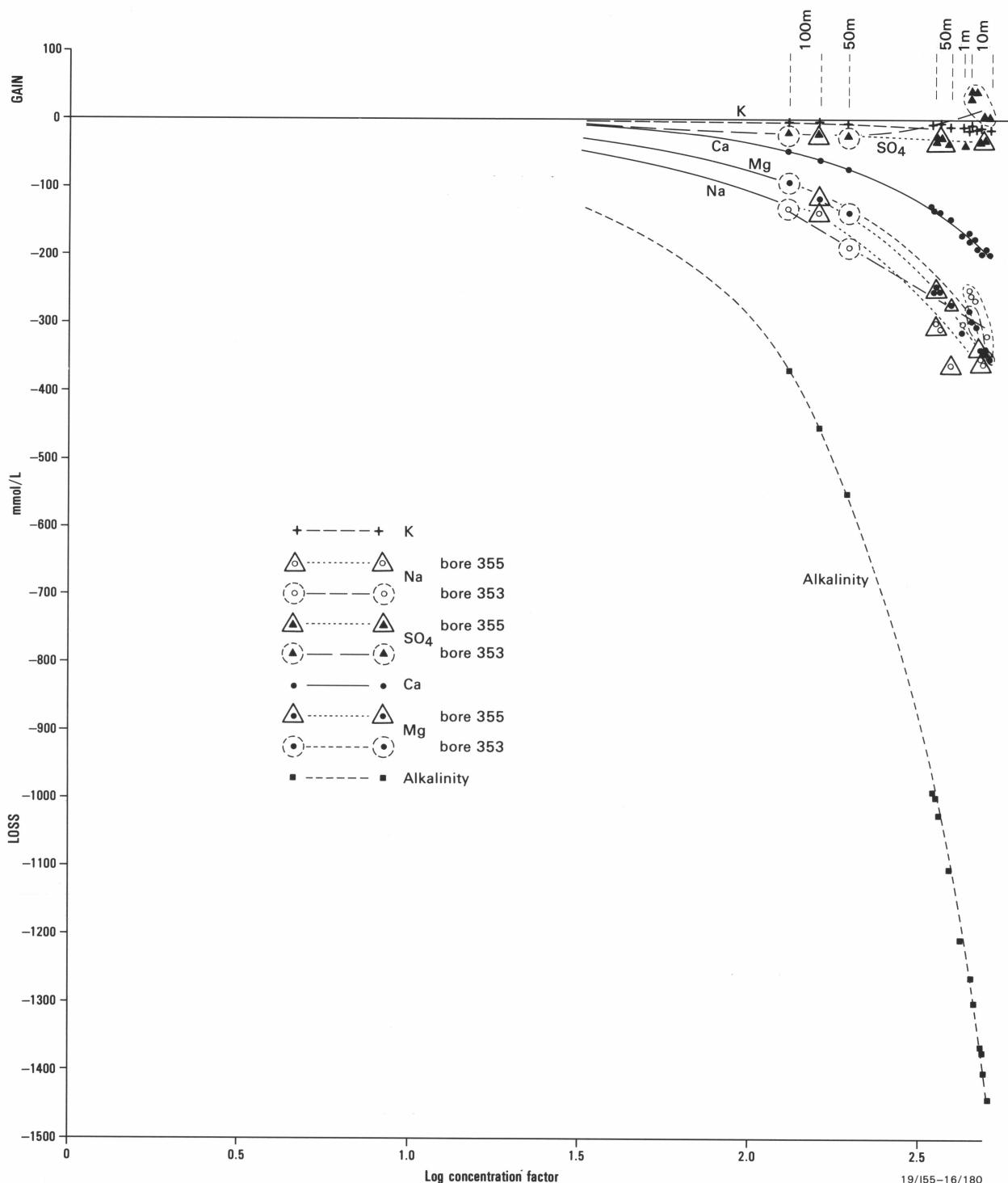


Figure 24. Ion transfer as a function of chloride concentration factor, lake-bed groundwaters.

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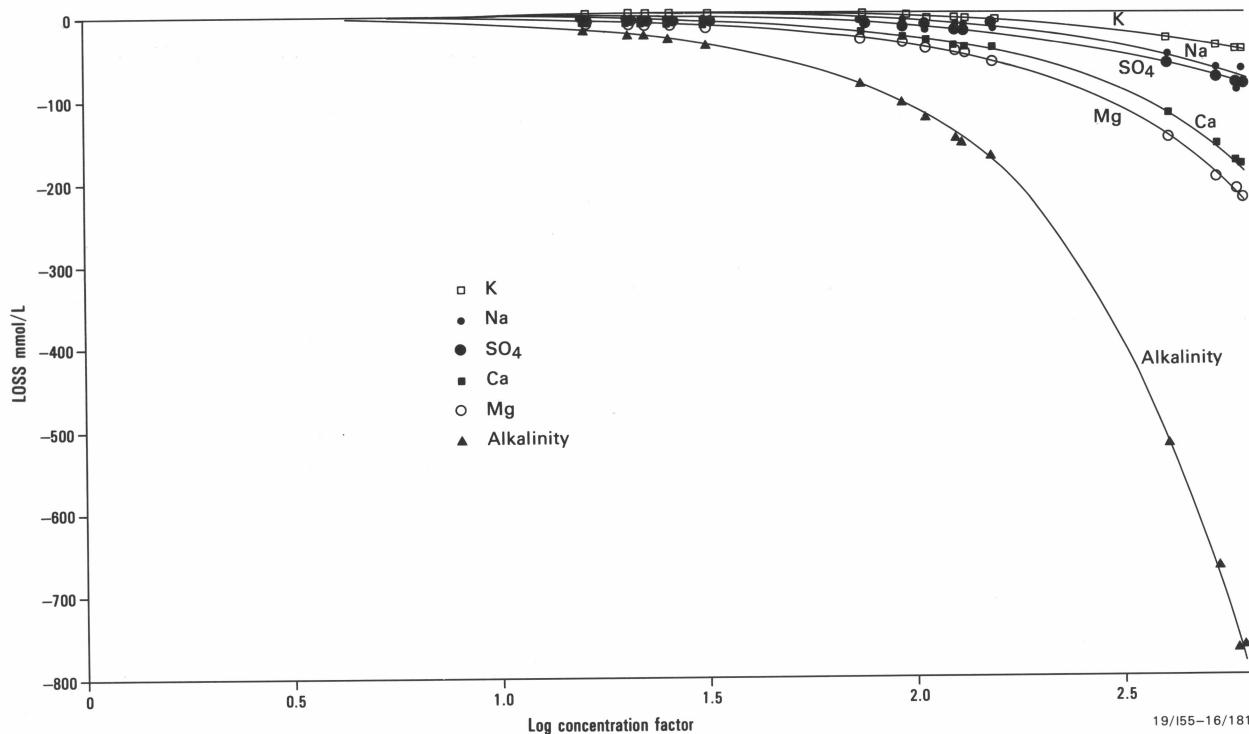


Figure 25. Ion transfer as a function of chloride concentration factor, lake waters.

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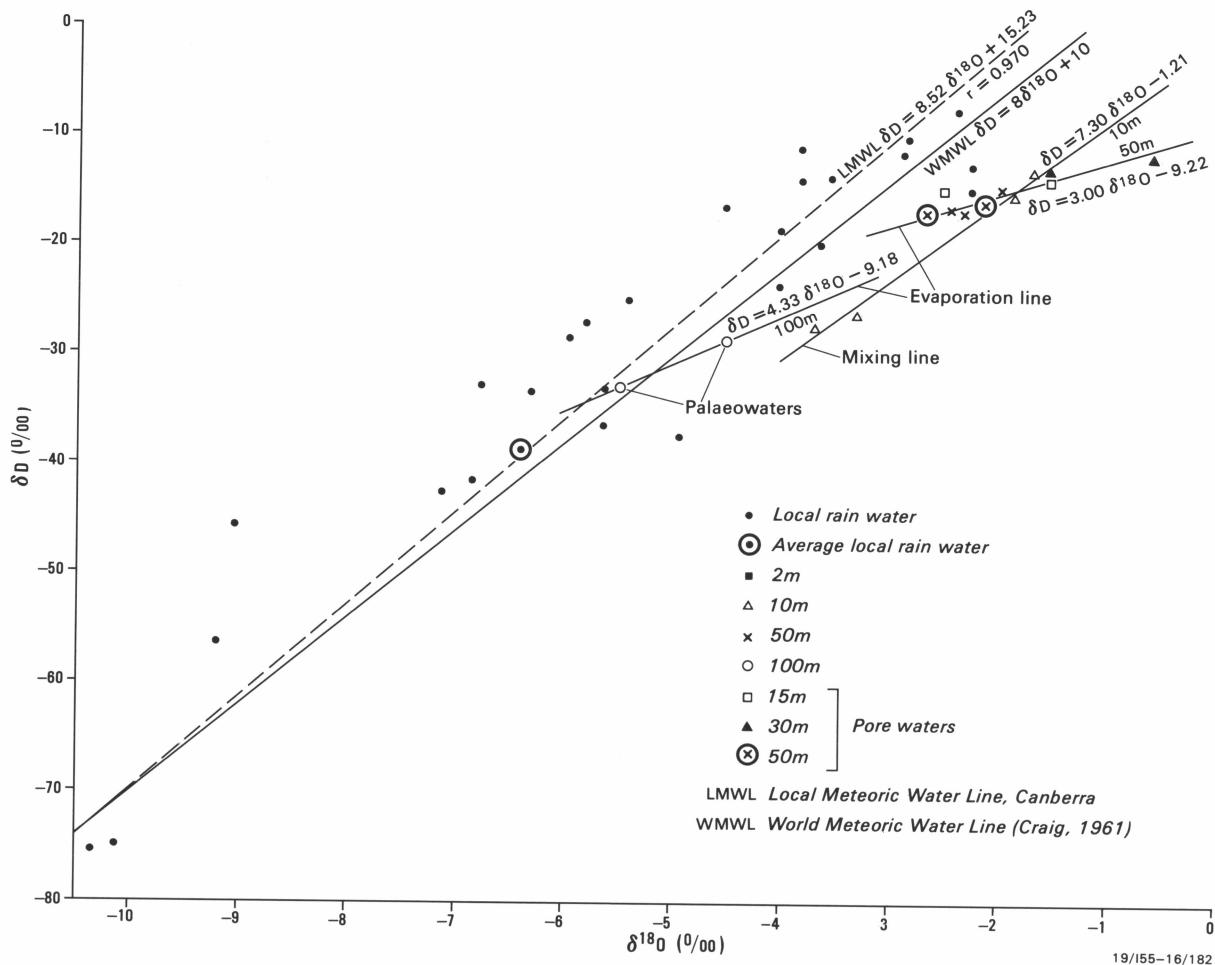


Figure 26. Relationships between stable isotope contents of rainwater and groundwater.

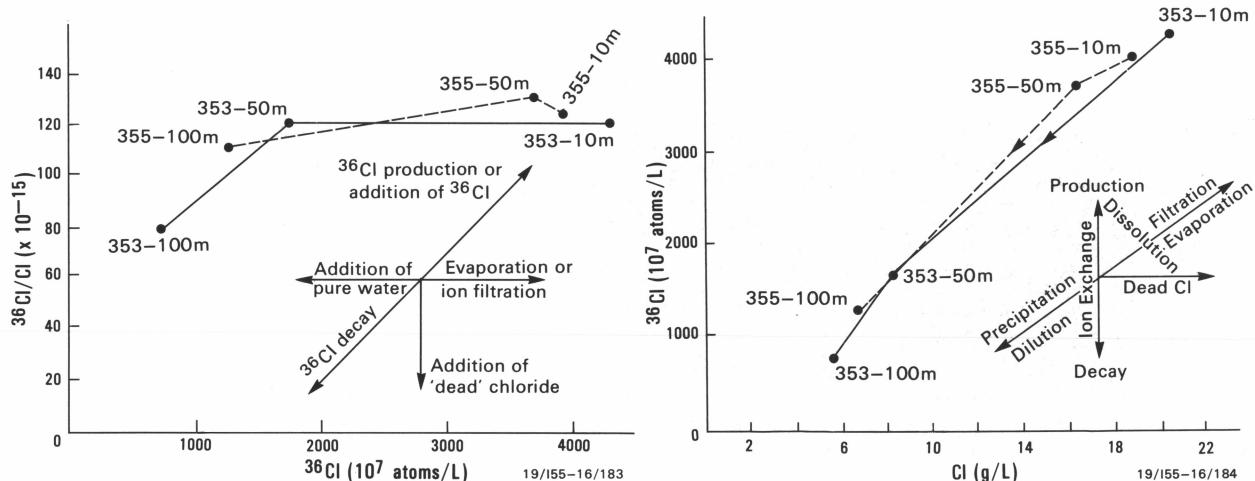


Figure 27. Relationship between $^{36}\text{Cl}/\text{Cl}$ ratio and ^{36}Cl concentration in lake-bed groundwaters.

Figure 28. Relationship between ^{36}Cl and Cl concentrations in lake-bed groundwaters.

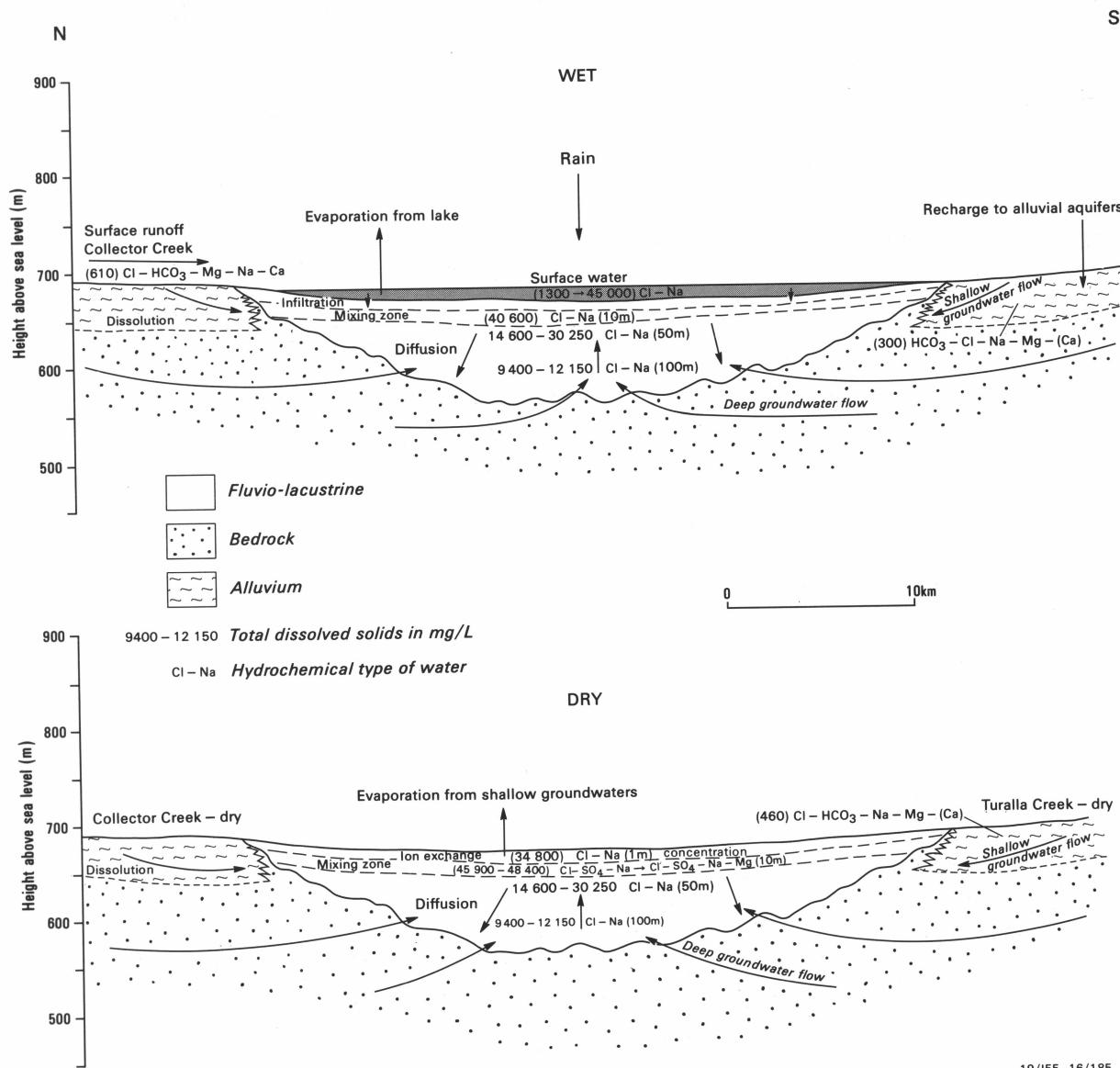


Figure 29. Processes in the wet and dry cycles of Lake George.

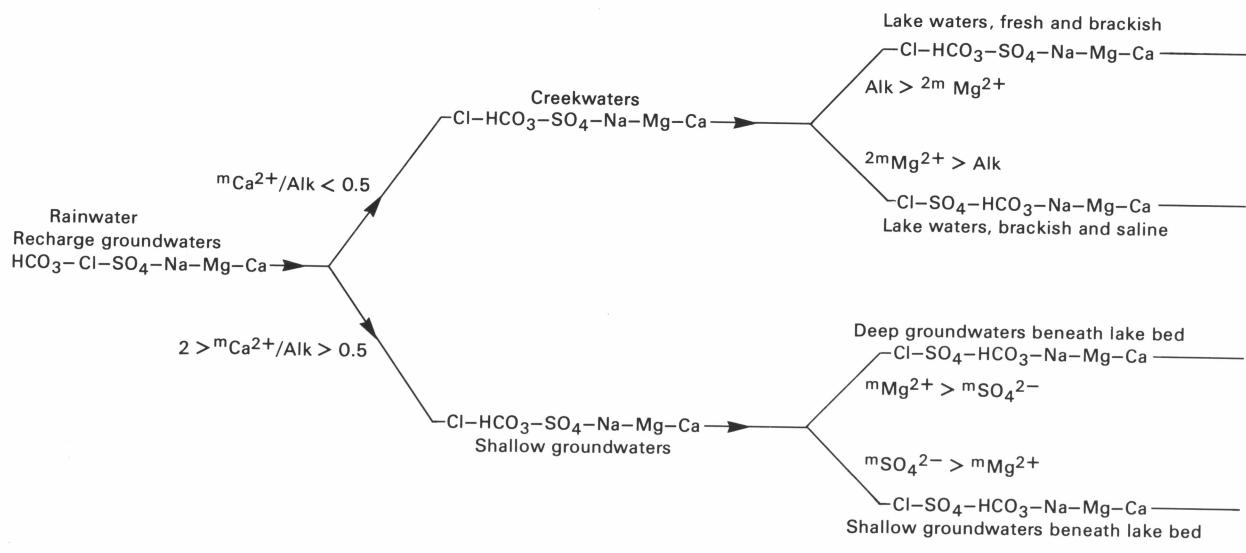


Figure 30. Possible model for hydrochemical evolution.

