Controls on the chemical composition of groundwater from alluvial aquifers in the Wanaka and Wakatipu basins, Central Otago, New Zealand

Michael Rosen · Sarah Jones

Abstract Groundwater in alluvial aquifers of the Wakatipu and Wanaka basins, Central Otago, New Zealand, has a composition expressed in equivalent units of $Ca^{2+} \gg Mg^{2+} \cong Na^{+} > K^{+}$ for cations, and $HCO_3^{-} \gg SO_4^{2-} > NO_3^{-} \cong Cl^{-}$ for anions. Ca^{2+} and HCO_3^{-} occur on a 1:1 equivalent basis and account for >80% of the ions in solution. However, some groundwater has increased proportions of Na^{+} and SO_4^{2-}, reflecting a different source for this water.

The rock material of the alluvial aquifers of both basins is derived from the erosion and weathering of metamorphic Otago Schist (grey and green schists). Calcite is an accessory mineral in both the grey and green schists at <5% of the rock. Geological mapping of both basins indicates that dissolution of calcite from the schist is the only likely mechanism for producing groundwater with such a constant composition dominated by Ca^{2+} and HCO_3^{-} on a 1:1 equivalent basis. Groundwater with higher proportions of Na^{+} and SO_4^{2-} occurs near areas where the schist crops out at the surface, and this groundwater represents deeper and possibly older water derived from basement fluids. Anomalously high K^{+} in the Wakatipu basin and high NO_3^{-} concentrations in the Wanaka basin cannot be accounted for by interaction with basement lithologies, and these concentrations probably represent the influence of anthropogenic sources on groundwater composition.

Résumé Dans les aquifères alluviaux des bassins de Wakatipu et de Wanaka (Otago central, Nouvelle-Zélande), la composition chimique des eaux souterraines peut être résumée ainsi, en équivalents: $Ca^{2+} \gg Mg^{2+} \cong Na^{+} > K^{+}$ pour les cations, et $HCO_3^{-} \gg SO_4^{2-} > NO_3^{-}$ et Cl^{-} pour les anions. En équivalents, le rapport entre Ca^{2+} et HCO_3^{-} est de l'ordre de 1; ces ions représentent plus de 80% des ions présents dans la solution. Cependant, une partie de ces eaux souterraines possède des teneurs plus élevées en Na^{+} et SO_4^{2-}, ce qui traduit une origine différente.

Les matériaux constituant les aquifères alluviaux de ces deux bassins proviennent de l'érosion et de l'altération des schistes métamorphiques d'Otago (schistes gris et verts). La calcite est un minéral accessoire présent pour moins de 5% aussi bien dans les schistes gris que dans les verts. La cartographie géologique des deux bassins montre que la dissolution de la calcite des schistes est le seul mécanisme possible pour donner à l'eau souterraine une composition chimique aussi constante et caractérisée par un rapport 1 entre Ca^{2+} et HCO_3^{-}. L'eau souterraine possédant les plus fortes teneurs en Na^{+} et en SO_4^{2-} est présente près des zones où affleurent les schistes; cette eau souterraine est une eau d'origine plus profonde et probablement plus ancienne, provenant du substratum. Les concentrations anormalement fortes en K^{+} dans le bassin de Wakatipu et les concentrations élevées en NO_3^{-} dans celui de Wanaka ne peuvent pas être attribuées à une interaction avec les roches du substratum; de telles teneurs correspondent probablement à l'influence anthropique sur la composition de l'eau souterraine.

Resumen Las aguas subterráneas en los acuíferos aluviales de las cuencas de Wakatipu y Wanaka, en Central Otago, Nueva Zelanda, tienen una composición química de manera que, expresándolos en términos de en equivalentes, los iones se pueden ordenar como $Ca^{2+} \gg Mg^{2+} \cong Na^{+} > K^{+}$ para los cationes, y $HCO_3^{-} \gg SO_4^{2-} > NO_3^{-} \cong Cl^{-}$ para los aniones. Ca^{2+} y HCO_3^{-} presentan una equivalencia 1:1, y entre los dos suponen más del 80% de los iones en disolución. Sin embargo, algunas aguas subterráneas presentan cantidades mayores de Na^{+} y SO_4^{2-}, lo que refleja una procedencia diferente.

El material rocoso de los acuíferos aluviales en ambas cuencas procede de la erosión y la alteración del Esquisto de Otago (esquistos grises y verdes). La calci-

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ta es un mineral presente en ambos esquistos, aunque con proporciones menores del 5%. Los mapas geológicos de ambas cuencas indican que la disolución de calcita procedente de los esquistos es el único mecanismo probable para producir unas aguas subterráneas con una composición tan constante de carbonato cálcico. Aguas subterráneas con mayores contenidos de Na^+ y SO_4^{2-} tienen lugar en zonas donde los esquistos afloran en superficie, por lo que estas aguas son más profundas y más viejas y provienen de circulación profunda, por la base del acuífero. Valores anormalmente altos de K^+ en la cuenca de Wakatipu y de NO_3^- en la de Wanaka no pueden justificarse por la interacción con los materiales de la base del acuífero, por lo que estas concentraciones están probablemente influenciadas por fuentes antrópicas.

Key words New Zealand · hydrochemistry · groundwater quality · metamorphic rocks · unconsolidated sediments

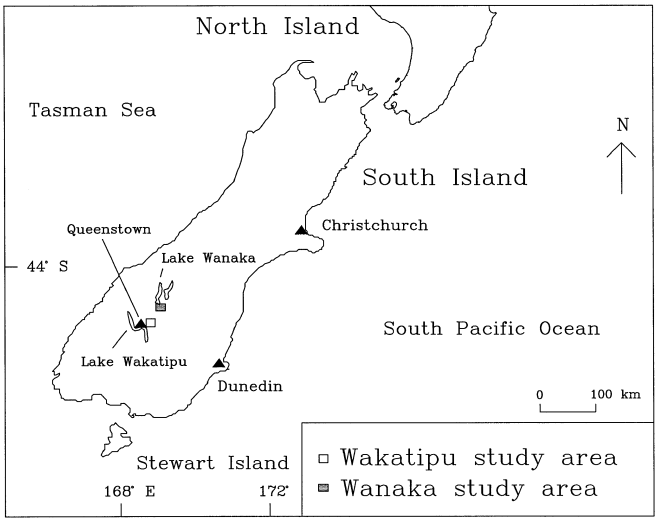

Fig. 1 Location of the Wakatipu and Wanaka basins in Central Otago, South Island, New Zealand

Introduction

The Wanaka and Wakatipu basins, Central Otago, are located in mountainous areas near major river and lake systems on the south Island of New Zealand; locations are shown in *Figure 1*. The major hydrological influences on the distribution of groundwater in the basins are the extent of sedimentary deposits formed from Pleistocene-age glaciation and the continuing processes of alluvial-fan and river deposition. Almost all of the groundwater extracted in both study areas is obtained from unconsolidated sediments (river gravels, scree deposits, and glacial outwash) derived from metamorphosed schist that provides the regional basement for the area.

The use of groundwater as drinking and irrigation water has been increasing steadily in these basins over the years as more people move to so-called 'lifestyle' blocks that are not served by the public water supplies of the towns of Wanaka and Queenstown, directly west of the Wakatipu basin. These public water-supply systems are fed by water from lakes Wanaka and Wakatipu, respectively, and other small local systems are fed by various river waters, especially in the Wakatipu basin. However, little is known about the variations in groundwater quality in either basin, and no systematic study has been conducted to address this issue. Indeed, there have been no detailed studies of the groundwater resources in the Wakatipu and Wanaka areas.

Close and McCallion (1988) conducted a regional survey of groundwater quality in the upper Clutha River valley, which includes the Wanaka basin, to determine the likely effects of the Clutha hydroelectric development. They included the water quality of eight water wells in the Wanaka area, but only one that is in the present field area, and observed that the composition of the groundwater was fairly consistent throughout the valley. No groundwater studies on water quality in the Wakatipu area are known to the authors.

The present study was initiated to determine: (1) variations in chemical composition and flow directions of groundwater; (2) lithological controls on the chemical composition of groundwater; (3) baseline conditions of water quality from which future measurements could be compared; and (4) the age of the water. This paper focuses on the first two objectives of the study and presents hydrochemical information on wells from both basins and compares this with results of basement and surficial lithological mapping. The purpose of this paper is to assess the chemical controls on groundwater composition in the basins and to determine if natural variations in chemical compositions exist that may indicate multiple sources of groundwater to the basins. The overall similarity of the basement rocks in the two basins indicates that any differences in the chemical composition of groundwater in the two basins are probably due to local differences and are not necessarily the result of regional weathering or erosion patterns.

Physical Setting

Location

Both the Wanaka and Wakatipu basins occur along the spine of the Southern Alps surrounded by snow-capped mountains. The area studied in the Wanaka Basin, shown in *Figure 2A*, extends from the mountainous terrane to the south of Wanaka township, the Clutha River to the north, and is bounded by Lake Wanaka to the west. The study area in the Wakatipu Basin, shown in *Figure 2B*, is bounded by the Shotover River to the west, the Arrow River to the east, Arrowtown to the north, and the Kawarau River to the south. These areas encompass most of the wells drilled in the basins.

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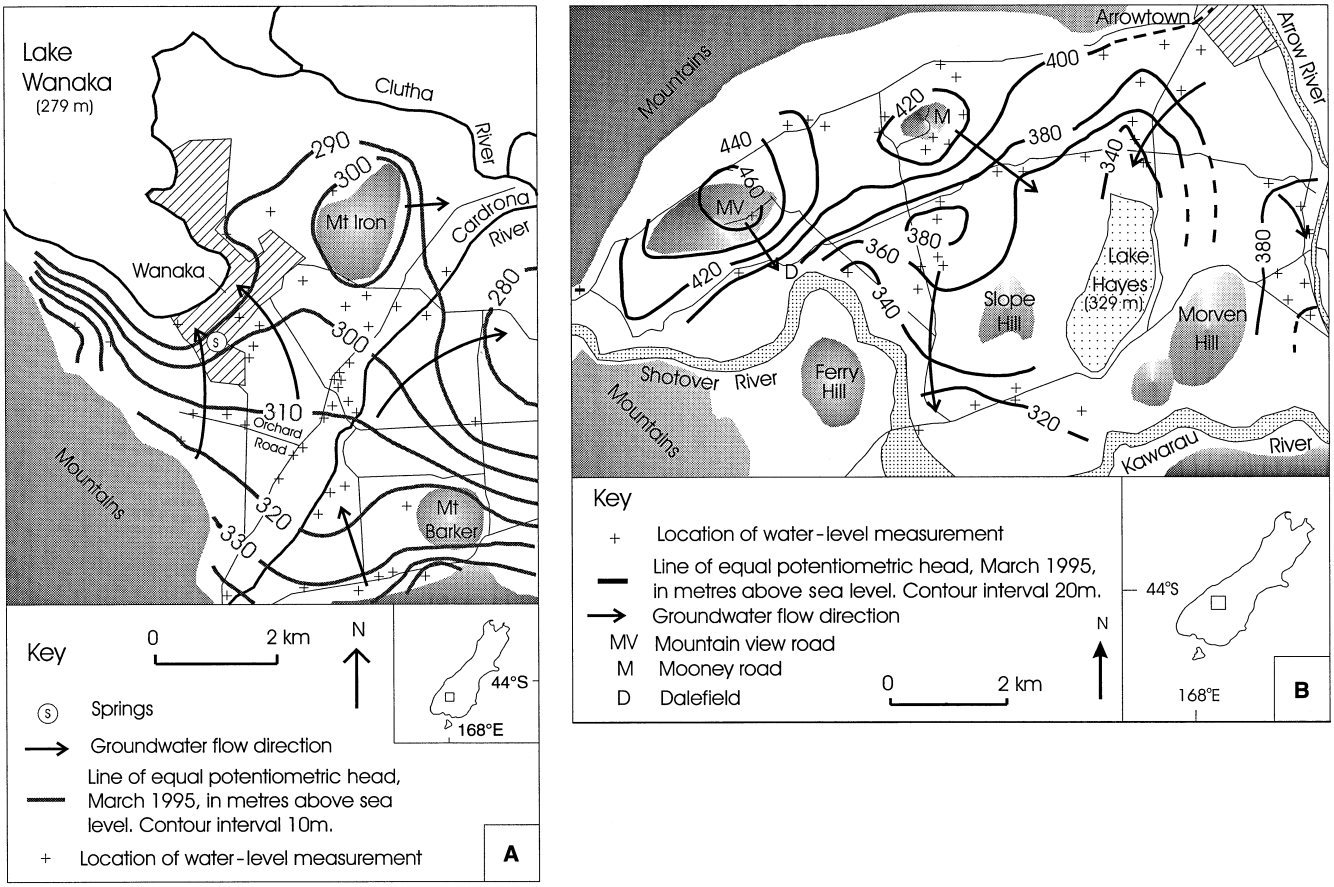

Fig. 2A, B Well locations used for water-level measurements. **A** In the Wanaka basin; **B** in the Wakatipu basin, showing the potentiometric surface, early March 1995

Climate

Climatic zones based on average rainfall and on soil types in areas where sufficient meteorological information was not available indicate that the Wanaka basin is dominantly subhumid. Rickard and Cossens (1968) indicate that the Arrow basin (equivalent to the Wakatipu basin) is subhumid in the middle of the basin but humid near the mountains and Lake Wakatipu.

The Wakatipu basin receives on average 135 mm more rain than the Wanaka basin. Average annual precipitation for the Wakatipu basin, based on 105 years of collection, is 818 mm; minimum yearly precipitation is 543 mm and maximum is 1298 mm. In the Wanaka basin, the average annual precipitation based on 59 years of collection to 1990 is 682 mm; minimum is 419 mm and maximum is 954 mm. In 1995, the Wanaka basin received 1310 mm of precipitation for the year, much above the yearly average. However, the collection site had been moved from a point near Lake Wanaka to a site along the Clutha River. The movement of the site may have influenced the precipitation data for 1995; nevertheless, the amount of precipitation in the Wanaka basin during the study period (1995) was very high and similar to the amount and pattern of precipitation recorded in 1995 for the Wakatipu basin (1243 mm).

No predictable seasonal precipitation patterns have been discerned in either basin. Any given month may receive anything from a few millimetres of precipitation to about 200 mm, and average monthly precipitation data are generally within about 30 mm of each other (Rosen et al. 1997). Rainfall generally falls from fronts brought to Central Otago by winds from the westerly quarter. Data on the chemical composition of rainfall in the Wanaka and Wakatipu basins are lacking.

Evaporation measurements from Wanaka and Wakatipu are not available. However, measurements from Tara Hills, approximately 80 km north of Wanaka, indicate that evaporation exceeds rainfall on a yearly basis. The estimated open-water evaporation rate for this area is 960 mm, and the rainfall is 530 mm (Finkelstein 1961). Similar evaporation rates would be expected from Wanaka and Wakatipu, because Tara Hills has rainfall amounts and an alpine climate that are similar to those of Wanaka.

Soils

Leamy and Saunders (1967) and Rickard and Cossens (1968) mapped the distribution of soils in the Wanaka and Wakatipu basins, respectively. In the humid to subhumid areas near the lakes, the soils are classed as sub-

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hygrous yellow-grey earths or dry hygrous yellow-brown earths. Clay pans and hard pans are lacking and the texture is silty (Rickard and Cossens 1968). The area around Wanaka is dominated by sandy loam soils with low cation exchange capacity and slightly acidic pH, and no carbonate deposition occurs in the C-horizon of these soils (Leamy and Saunders 1967).

Land Uses

Land uses in the Wanaka basin are dominated by typical high-country rural livestock farming. The main herds are sheep and deer, but smaller holdings of cattle and horses are also present. A public golf course is also present in the study area. Extensive horticulture is not present in the Wanaka basin. Land uses in the Wakatipu basin are more varied than in Wanaka and include a similar mixture of sheep and deer farms. However, vineyards and orchards are also important land uses in the Wakatipu basin. A golf course is also present in the study area of the Wakatipu basin. Detailed land-use maps are not available for either basin.

Geology

The Otago Schist forms the basement rocks in the Wakatipu and Wanaka basins. These rocks are of Permian and Triassic age and represent regionally metamorphosed quartzofeldspathic sandstones and argillites with minor basalts, cherts, and limestones, which formed in a Mesozoic collision zone between three metasedimentary terranes (Norris and Craw 1987; Turnbull and Forsyth 1988; Mortimer 1993). Parent sedimentary-rock compositions have only minor local variations throughout Otago, and the schist is therefore subdivided and mapped on the basis of textural parameters (e.g., Bishop 1972) and some marker lithologies (e.g., Wood 1962; Turnbull 1988). Most of the schist in the Wakatipu and Wanaka basins is textural zone IV, with only minor textural zone III in small infaulted areas of schist in the foothills of the Remarkables, Wakatipu Basin (Cox 1991) and in scattered localities in the Wanaka area (Craw 1984).

Otago Schist

The Otago Schist consists of two main rock types: (1) quartzofeldspathic schist, or greyschist, which represents metamorphosed sedimentary rocks; and (2) greenschist, which is derived from metavolcanic material. The distributions of the geological units are shown in *Figure 3A,B*. The greyschists are further subdivided into (1) psammitic schist, composed of the metamorphic mineral assemblage quartz-albite ± epidote-chlorite-

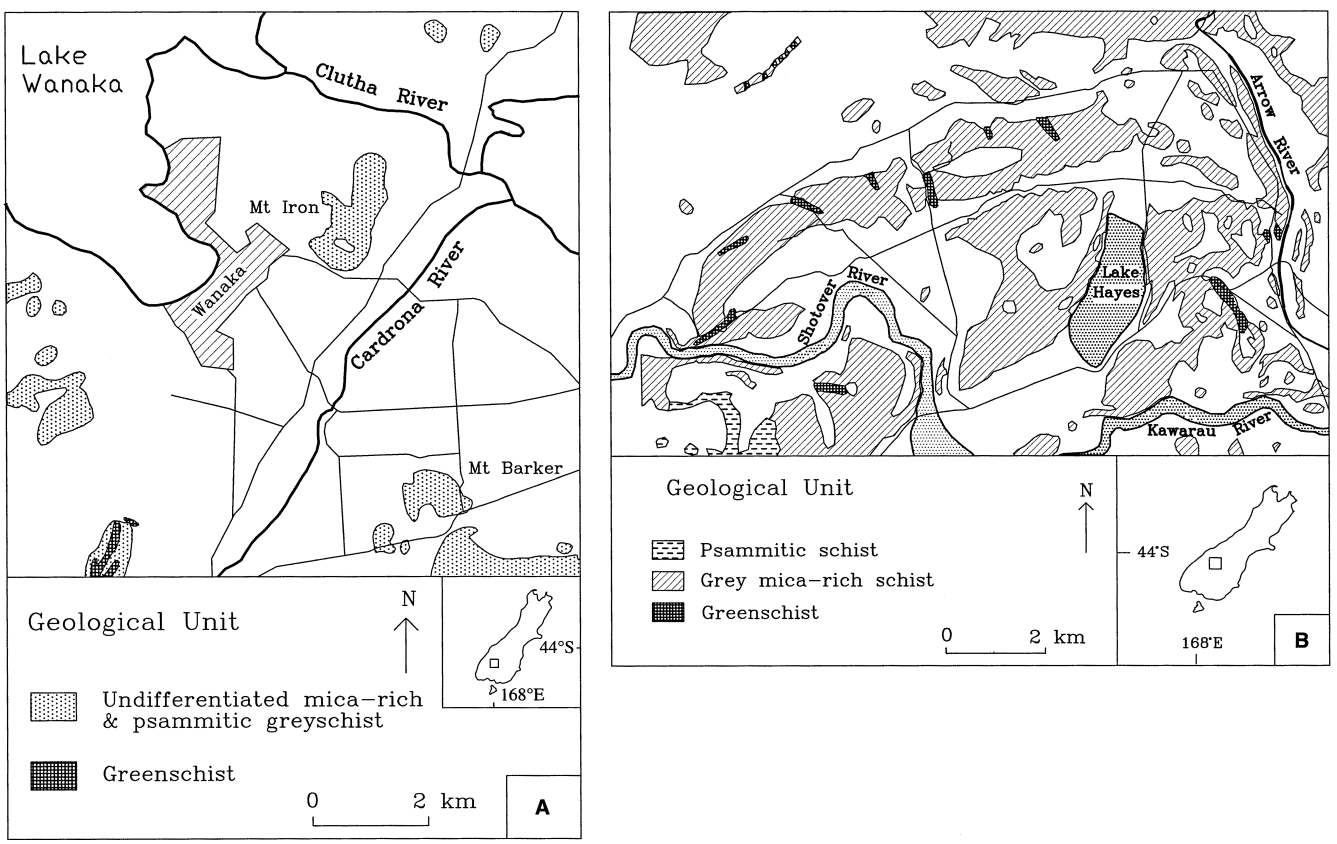

Fig. 3A, B Bedrock-outcrop maps of **A** the Wanaka basin and **B** the Wakatipu basin

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muscovite-calcite and muscovite-chlorite ± actinolite-epidote-biotite-titanite-quartz-albite; and (2) grey pelitic (mica-rich) schist, composed of muscovite-chlorite-albite-quartz-epidote-actinolite-calcite-titanite. Hutton (1940) gives detailed petrographic descriptions of the various schist lithologies, and Craw (1984) and Mortimer (1993) give good summaries of the different schist types.

Greenschist is composed of albite-epidote-chlorite-titanite with minor magnetite (or pyrite and pyrrhotite), actinolite, stilpnomelane, biotite, quartz, muscovite, calcite, and apatite in various proportions (Mortimer 1992; Craw 1984). In the Wakatipu and Wanaka basins, greenschist is common but volumetrically minor (<10%), and occurs as bands (1 cm to >100 m thick) interlayered with the quartzofeldspathic schists. Most greenschist bands are laterally extensive for many mertes and commonly contain much calcite (Craw 1984). Weathered carbonate pits are also prominent in some greenschist rocks.

Scattered occurrences of serpentinite are also present in the Wakatipu basin. Serpentinite consists of metamorphosed basic–ultrabasic intrusive rocks in which differential igneous layering developed prior to metamorphism. The serpentinite consists of layers of talc-antigorite-tremolite-dolomite-biotite-chlorite, calcite-chlorite-actinolite-epidote-biotite, and albite-chlorite-calcite-epidote-biotite schist (Craw 1984; Turnbull 1988). A serpentinite body occurs near the head of Spring Burn in the Wakatipu area (Cooper 1976). Other very small serpentinite bodies are scattered throughout the Wakatipu basin. This lithology has not been reported in the Wanaka study area, although some rocks have ultramafic affinities (Craw 1984).

Mineralisation associated with the metamorphism has produced a variety of minerals of economic and sub-economic value in the area, such as gold, various sulphides, manganese-bearing cherts (Coombs et al. 1985), and metamorphic calcite. The variety of ions available from weathering of the basement rocks has important implications for the chemical composition of the aquifers.

Tertiary-Age Sediments

Small Tertiary-age (Upper Oligocene to Pliocene) sedimentary remnants of marine and lacustrine origin (limestones, sandstones, mudstones, and lignite) occur outside of both basins (Wood 1962; Barrell et al. 1994), but the locations of these deposits are scattered and the volume of sediments is small. The most significant limestone deposit is an Oligocene-age marine limestone located at Bob's Cove, which is about 15 km southwest of the Shotover River in the Wakatipu basin (Turnbull et al. 1975). The deposit extends as narrow patches in a general north-south direction 40 km to the upper Shotover River along the Moonlight Fault, but it does not occur in the present study area.

Quaternary-Age Sediments

The distribution of groundwater in both the Wanaka and Wakatipu basins is controlled by the deposition of alluvial-fan and river sediments, and by the distribution of glacially derived deposits formed during the Pleistocene Epoch. Almost all of the groundwater extracted in both study areas is obtained from unconsolidated sediments, which are derived mostly from the Otago Schist. A few wells derive their water from fractured-rock aquifers in the schist.

In the Wakatipu basin, the irregular relief of the basement schist surface below the sediments surrounding the Wakatipu area has broken the alluvial aquifers into small units whose interconnectivity is unknown. Barrell et al. (1994) mapped the surficial deposits in the Wakatipu Basin and demonstrated that a complex mixture exists of small aquifer units of unknown thicknesses and extents. The hydrology of the area is further complicated by significant human modification of surface-water conditions by the construction of irrigation channels and by the draining of wetland areas around Lake Hayes. The aquifers are composed of glacial deposits that contain a significant proportion (as much as 30%) of greywacke gravel from the Caples Group sediments (Barrell et al. 1994) and colluvium, alluvium, stream, and river sediments derived from greywacke and the Otago Schist. Sediments range in type from poorly sorted gravels and sands to fine sands and silts.

In the Wanaka basin, Thomson (1976) mapped the extent of glaciation, constructed cross sections of the alluvial deposits, and provided information on groundwater flow directions. The surficial deposits in the Wanaka basin have a less complicated structure, because the Cardrona River acts as a distribution source over the glacially deposited sediments. The compositions of the sediments are similar to those of the Wakatipu basin, but because sediments of the Caples Group are not present in the study area, most of the alluvial and glacial sediments are derived directly from the surrounding schists. The geological structure and sedimentology of the surficial deposits of the Wanaka basin are currently under investigation (I. Turnbull, pers. comm. 1995).

Methods

Hydrogeologic Studies

Basement mapping of the Wanaka and Wakatipu areas had not been done in any detail prior to this study. However, studies by Cox (1991), Cotton et al. (1991), and Mortimer (1992, 1993) provide information on some specific areas of the region. In order to determine if a correlation exists between bedrock lithology and groundwater composition, geological mapping of the outcrops was carried out in both basins (*Fig. 3A,B*). Lithological variations and foliation attitudes within the schist were mapped, and quartz veins were investigated for presence/absence of calcite (see below).

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Lithological details of borehole logs from both basins were also investigated from drillers' logs held at the Otago Regional Council (ORC). Geological information was obtained for 50 bores in both basins, 31 in the Wanaka basin and 19 in the Wakatipu basin. These data indicate that the average depth of bores in the Wanaka basin is 37 m; the range is 20–91.7 m. In the Wakatipu basin, the average bore depth is 32 m (range 2.7–73.7 m total depth). A total of 13 bores penetrate basement rocks, three in Wanaka and ten in Wakatipu. The alluvial sediment cover is thinner in the Wakatipu basin than in the Wanaka basin, based on the average depth of bores, more abundant outcrops in the Wakatipu basin, and the much higher percentage of bores in basement rocks in the Wakatipu basin.

Groundwater bores and wells were located in the Wakatipu and Wanaka areas from ORC files, drilling permits, and site visits. A total of 82 bores in the Wanaka area and 58 bores in the Wakatipu area were surveyed by the Department of Survey and Land Information (DOSLI) using a Fast Rapid Static Global Positioning System (GPS). A baseline reference site was established in a relatively central location in each basin, and the remaining two receivers were used to collect data for a minimum of 5 min at each site. Accuracy of this method is better than ± 0.10 m for coordinate points as much as 20 km apart. Water levels in 47 bores in Wanaka and 46 bores in Wakatipu were measured from the surveyed bores in May, 1995. The distribution of bores in both basins is non-uniform, and so potentiometric-surface maps constructed from these data are limited to areas of adequate well density (*Fig. 2A*,*B*).

Water Sampling and Analysis

Water samples were collected on five occasions from domestic water bores and wells that were in use. In the Wanaka basin, almost all bores consist of narrow-diameter (<100 mm), stainless-steel or PVC-cased pipe with a submersible pump at the screen depth. In the Wakatipu basin, some groundwater samples were taken from older wells (approximately 0.5–1 m in diameter) supplied with submersible pumps or suction pumps. All samples were taken as close to the well head as possible and before any pressure cylinders or reticulation to the houses. Conductivity, temperature, and pH were measured in the field and allowed to stabilise before sample collection. Samples were field-filtered with a 0.45-mm Millipore filter and acidified with Ultrapur Merck nitric acid for cation analyses; field-filtered and chilled below 4 °C for nutrient and anion analyses; and unfiltered and chilled below 4 °C for alkalinity measurements.

A preliminary sampling trip was conducted in August, 1994, and one river water and 12 groundwater samples were analysed at the Institute of Geological and Nuclear Sciences Analytical Facility using a Technicon Auto Analyzer for anions and a Perkin Elmer 1100 atomic absorption spectrophotometer for cations. In each of March, June, September, and December, 1995, 20–40 water samples were collected in each basin. A total of 47 bores/wells were sampled in the Wanaka basin and 46 bores/wells were sampled from the Wakatipu basin. Most of the samples were analysed by ESR Ltd. in Christchurch for inorganic constituents, but, for comparison, some were analysed at the Institute of Geological and Nuclear Sciences Ltd. Analytical Facility in Wairakei. A full listing of the chemical results is contained in Rosen et al. (1997), and representative analyses are listed in *Tables A1* and *A2*, in the Appendix at the end of this article. Cation/anion balances were used to determine if the analyses were acceptable.

All samples were analysed for major cations and anions (Na^+, Ca^{2+}, Mg^{2+}, K^+, Cl^-, SO_4^{2-}, HCO_3^-) and most were analysed for nutrients, namely, dissolved reactive phosphorus (DRP) and nitrate + nitrite (NNN). Conductivity, pH, and water temperature were measured in the field from a steady stream of water from the bores. A variety of techniques was used to analyse the samples, including: flame atomic absorption (Na^+, Ca^{2+}, Mg^{2+}, K^+); auto titration (HCO_3^-); Auto Analyzer (nutrients); and ion chromatography (Cl^-, SO_4^{2-}). Samples of the Arrow River near Arrowtown and the Cardrona River near Mt. Iron were also analysed for the same parameters, except DRP. The samples collected in August, 1994, were also analysed for monomeric silica using the Technicon Auto Analyzer.

Results

Groundwater Flow Directions

Groundwater flow directions in both basins are complex due to the high relief of the mountains enclosing the basins and the influence of glacially eroded topography on the distribution of aquifer sediments. The Wanaka basin is less complex than the Wakatipu basin and has a better distribution of bore locations.

Wanaka Basin

The Cardrona River valley is constrained by steep-sided mountains from its headwaters to the beginning of the Wanaka basin. Groundwater from the area upstream of the Wanaka basin flows toward the river at a steep gradient (>10 m/km). As the river valley opens out into the Wanaka basin, the gradient of both the river and the groundwater lessens and groundwater begins to move away from the river somewhere near Orchard Road (groundwater gradient is about 6 m/km). At this point, groundwater west of the river moves toward Lake Wanaka and supplies water to the springs that crop out around the town site (*Fig. 2A*). East of the river, past Orchard Road, groundwater flows toward the northeast and eventually to the Clutha River *(Fig. 2A*). Depth to groundwater is shallowest (<5 m) near the Cardrona River and Lake Wanaka but ranges from 5–20 m elsewhere in the basin.

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Mt. Barker and Mt. Iron, which are both schist-cored roche moutonées, act as small recharge areas, which complicates evaluation of groundwater flow directions in these areas. On the eastern slopes of Mt. Iron, groundwater flow is back to the Cardrona River, and on the southern slopes groundwater flow is to the south, creating a groundwater divide between water flowing toward the Wanaka town site and water flowing toward the Cardrona River.

Thomson (1976) correctly inferred the groundwater flow in the area of the Wanaka town site to be from the Cardrona River and that the line of springs surrounding the town (*Fig. 2A*) was recharged mostly from the Cardrona River. The springs occur where a compact and relatively impermeable glacial till crops out (Thomson 1976). A confined aquifer, penetrated by a farm-supply bore drilled to 25 m, may also exist below the unconfined surface aquifer (Thomson 1976), but this bore was drilled into gravel, and the static water in this bore is below the level of the Cardrona River. Due to a lack of a confining lithology and the low static water level, a confined aquifer is unlikely in this location and at this depth. No indication of confining pressures exists in any of the bores used to construct the potentiometric-surface map in the Wanaka basin.

Wakatipu Basin

The relief and structure of the Wakatipu basin and the irregular distribution of wells and bores in the area make the interpretation of groundwater movement in this basin difficult (*Fig. 2B*). Topographic highs at Morven Hill, Slope Hill, Mountain View Road, and Mooney Road cause groundwater mounds and effectively divide the Wakatipu basin into sub-basins with restricted water movement between basins. The Lake Hayes sub-basin is the best defined. Lake Hayes receives groundwater from all sides except the south (*Fig. 2B*) but is separated from the Arrow and Shotover River catchments by topographic highs and probable groundwater divides. Surface water and probably groundwater leave Lake Hayes to the south and enter the Kawarau River.

Unlike the Cardrona River, which loses water to the aquifer in the Wanaka basin, the steep gradient of the topography surrounding the Shotover, Arrow, and Kawarau Rivers means that groundwater flows into these rivers. One possible exception is at the junction of the Shotover and Kawarau Rivers (just south of Ferry Hill in *Fig. 2B*), where some surface water from the Shotover River could be lost to the ground under the Shotover delta. However, no groundwater measurements have been made in this area.

The middle of the Wakatipu basin is divided by a topographically high area defined by Slope Hill and the hill around Mooney Road (*Fig. 2B*). This is also a groundwater recharge area and separates groundwater from the Lake Hayes sub-basin and the Dalefield sub-basin. West of the Dalefield sub-basin is the Shotover sub-basin, which is separated from Dalefield by a hill at Mountain View Road. At the east end of the Wakatipu basin is the Arrowtown sub-basin, which receives water from the Arrow River catchment and is separated from the Lake Hayes sub-basin by a basement topographic high at Morven Hill. Surface water and groundwater from all four of these sub-basins eventually flows to the Shotover and Arrow Rivers and then out of the basin through the Kawarau River to the east.

Depth to groundwater in the Wakatipu basin is, in general, shallower than in the Wanaka basin; most bores have a static water level of <10 m. In some places, such as south of Arrowtown (*Fig. 2B*), the depth to groundwater is <1 m. Thus, the Wakatipu basin as a whole is more vulnerable to land-use impacts than the Wanaka basin. The frequent use of drainage ditches to drain low-lying areas in the centre of the Wakatipu basin, particularly around Lake Hayes, confirms the high water table in the Wakatipu basin.

Groundwater Composition

The pH and temperature of groundwater are variable (pH = 5.3–8.6; T = 3.7–16.8 °C), and these measurements probably reflect the wide range of depths of the bores. Shallow bores (<5 m) are more likely to be influenced by climatic conditions during sampling than deeper ones. This is especially true for bores near river recharge areas. Lower pH values appear to be associated with areas where the Otago Schist crops out or is closer to the surface.

Major dissolved ions

All of the samples analysed are classified as calcium-bicarbonate water, as shown by the Piper diagram for both basins in *Figure 4*. Ionic equivalent abundances in both basins show that for cations: $Ca^{2+} \gg Mg^{2+} \cong Na^{+} > K^{+}$; and for anions: $HCO_3^{-} \gg SO_4^{2-} > NO_3^{-} \cong Cl^{-}$. Calcium and bicarbonate account for approximately 80% of the ions. NO_3^{-} and Cl^{-} account for only about 1 or 2% of the total ions in any given analysis, and depending on the well, nitrate may be greater than or less than chloride in abundance.

All ions in solution are enriched relative to a seawater concentration–dilution line, as shown in *Figure 5A–F*. However, Na^{+} appears to follow the slope of the line in the Wakatipu basin. Lower K^{+} concentrations in the Wanaka basin correspond to higher Na^{+} concentrations, but in many bores in the Wakatipu basin, higher K^{+} concentrations correspond to lower Na^{+} concentrations, as shown in *Figure 6*. K^{+} concentrations relative to Cl^{-} concentrations are similar in both basins (*Fig. 5D*). As shown in *Figure 7*, higher Na^{+} concentrations are associated with higher SO_4^{2-} concentrations in the Wanaka basin ($R^2 = 0.79$), but little correlation ($R^2 = 0.35$) exists in the Wakatipu Basin. A plot of milli-equivalent concentrations of Ca^{2+} to

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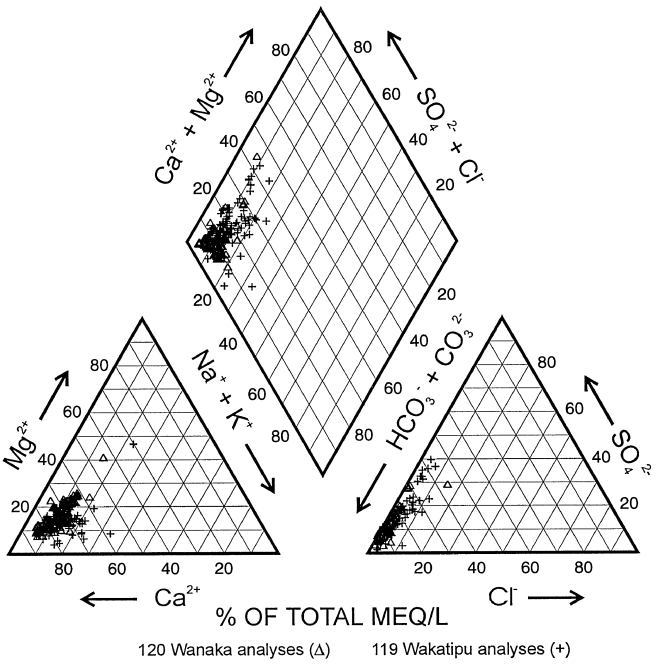

Fig. 4 Piper diagram of hydrochemical data in the Wanaka–Wakatipu basins

HCO_3^- in *Figure 8* shows that Ca^{2+} balances HCO_3^- on a nearly one-for-one equivalent basis. The slopes of the lines for each basin are near one (*Fig. 8*), and the Y-intercepts are near zero. When both basins are included in the correlation line, the slope of the line is 1.08, the Y-intercept is 0.05, and the $R^2 = 0.94$ ($N = 241$). When the basins are plotted individually the correlation is equally strong (*Fig. 8*). Equivalent Mg^{2+} to HCO_3^- correlations are not as strong as the Ca^{2+} to HCO_3^- correlations and the former correlation does not suggest a definitive relationship between Mg^{2+} and HCO_3^-.

The concentration of monomeric SiO_2 averages 11 g/m^3 in both basins; however, this average is based on only seven analyses in the Wanaka basin and five in the Wakatipu basin.

Nutrients

No simple correlation exists between DRP and Cl^- in either basin, as indicated by *Figure 9A*, but NNN concentrations correlate moderately with increased Cl^- concentrations ($R^2 = 0.90$) in the Wanaka basin (*Fig. 9B*). However, this correlation is strongly dependent on one point that has much higher nitrate and chloride concentrations than the rest of the data. When this point is removed, the correlation is not good ($R^2 = 0.32$). Nevertheless, a trend of higher chloride concentrations is accompanied by higher nitrate. Higher DRP concentrations do not correlate with higher NNN concentrations.

Temporal variations in the chemical composition of groundwater are not pronounced in either basin, and no definitive seasonal trends have been observed. However, one year of seasonal data is insufficient to definitively determine trends. More data are needed from consecutive seasons in multiple years to verify this observation.

Discussion

Chemical Types of Groundwater

The dominant ions in solution are Ca^{2+} and HCO_3^-, which occur on a one-for-one equivalent basis in both basins *(Fig. 8)*. With the exception of minor carbonate occurrences in the Wakatipu basin, no widespread limestone deposits occur in the area that could account for the dominance of calcium carbonate in solution at such a constant equivalent ratio in both basins.

Despite the dominance of Ca^{2+} and HCO_3^- in solution, samples from some bores have a higher proportion of Na^+ and SO_4^{2-} in the ion balance (*Fig. 7*). Locations of samples with higher SO_4^{2-} contents are shown in *Figure 10A,B*; they tend to be concentrated near outcrops of the Otago Schist. In the Wanaka basin, samples with higher SO_4^{2-} contents are near Mt. Barker, and in the Wakatipu basin they occur near Mooney Road and Morven Hill.

Sources of Ca^{2+} and HCO_3^-

Two sources may account for the relative abundance of Ca^{2+} in groundwater: (1) epidote-group minerals from the Otago Schist; and (2) minor, but ubiquitous, calcite, which occurs as an accessory mineral in almost all of the underlying schist. Although epidote-group minerals are abundant, weathering of epidote does not produce Ca^{2+} and HCO_3^- in a 1:1 equivalent ratio. In addition, the solubility of epidote-group minerals is low under earth-surface conditions, and the minerals are resistant to weathering in soils (Fitzpatrick 1984, p. 80). Calcite, on the other hand, is more soluble under earth-surface conditions and produces Ca^{2+} and HCO_3^- in a 1:1 equivalent ratio: $CaCO_{3(s)} + H_2O + CO_2 = Ca^{2+} + 2HCO_3^-$.

Calcite is an accessory mineral of the Otago Schist but is generally present in very small quantities, especially in the greyschists. Craw (1984, p. 154) provides point counts of four samples of porphyroblastic pelitic schist and observed only trace amounts of calcite in two samples, but 2 and 6.3 weight percent in the others. Calcite is an important accessory mineral in the greenschists, which most likely accounts for the generally higher Ca^{2+} content of these rocks.

Two data sets on the geochemistry of Otago Schist from Coombs et al. (1985) and Palmer et al. (1991) indicate that there are generally higher CaO values for greenschists compared to greyschists (pelitic and psammitic varieties). The CaO content of greyschists in the

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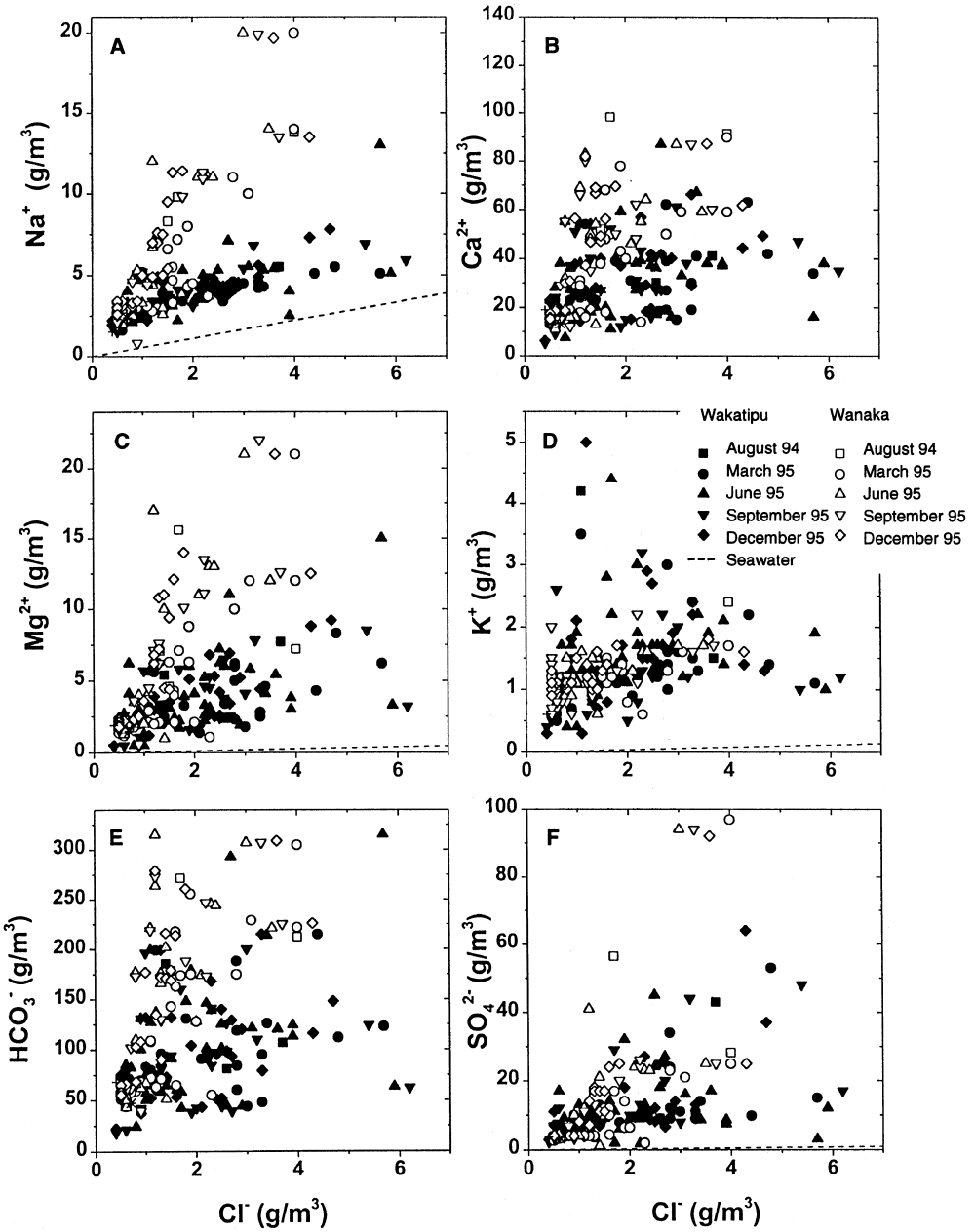

Fig. 5A–F Relation between Cl^- and other major ions. **A** Na^+; **B** Ca^{2+}; **C** Mg^{2+}; **D** K^+; **E** HCO_3^-; **F** SO_4^{2-}. A line representing the concentration or dilution of seawater composition is shown on all plots except those for Ca^{2+} and HCO_3^-. One sample from each basin is not plotted because each has a Cl^- concentration greater than 7 g/m^3. Cardrona River water is plotted as a (*). Arrow River water is plotted as a (+)

Wakatipu area ranges from 0.5 to just over 5.0 weight percent, whereas CaO in greenschists ranges from about 2.6–16.0 weight percent (the majority of greenschist samples plot above 8.0 weight percent). The higher Ca values for greenschists tie in well with the petrography, as epidote and calcite are common accessory minerals in greenschist but less so in the greyschists. This suggests that the volumetrically minor greenschists are a more abundant source of calcite than the predominant greyschists, but that greyschist may also contribute dissolved calcite to groundwater.

Evidence of calcite dissolution in groundwater recharge areas is provided by weathered schist that contains pitted impressions of former calcite crystals (Craw 1984). Processes that would contribute to the dissolution of calcite are the production of soil CO_2 by vegetation and the dissolution by rainwater that is undersaturated with respect to calcite. The calcic nature of the groundwater is illustrated by the presence of travertine-cemented gravels in the groundwater discharge areas around Kawarau Gorge down river from Arrow Junction (mapped by Turnbull 1988). Travertine is common in arid areas such as the Kawarau and Cromwell Gorges and is clearly visible on joint surfaces in bedrock roadcuts.

Because the occurrences of limestones in both basins are limited, they can be ruled out as a major source for Ca^{2+} and HCO_3^- in groundwater. But because calcite as an accessory mineral is more soluble than the dominant minerals in the Otago Schist, the chemistry of

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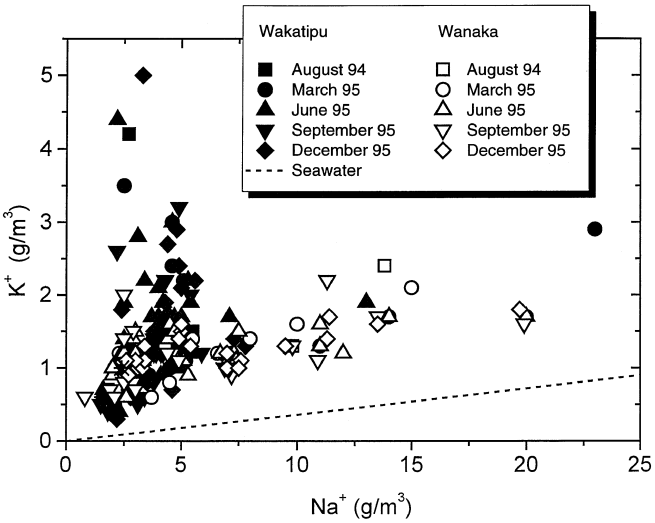

Fig. 6 Relation between K^+ and Na^+. Cardrona River water is plotted as a (*); Arrow River water is plotted as a (+). Seawater concentration–dilution line is shown for reference

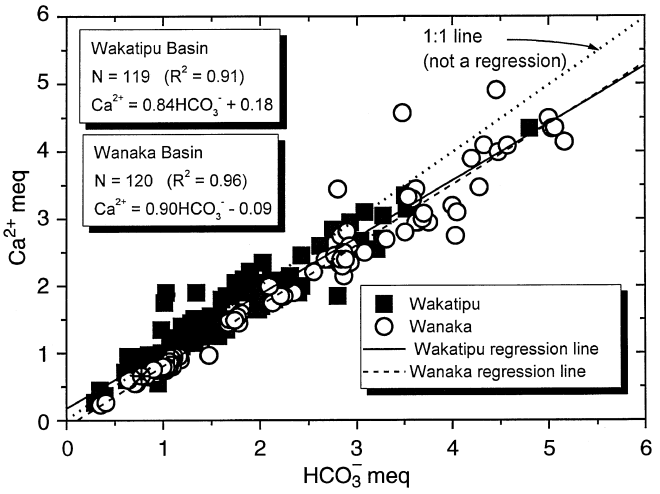

Fig. 8 Relation between Ca^{2+} and HCO_3^-, in milli-equivalents. Cardrona River water is plotted as a (*); Arrow River water is plotted as a (+)

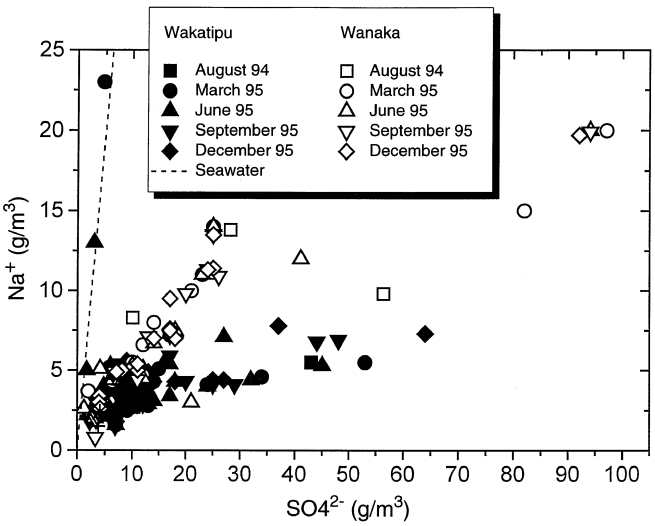

Fig. 7 Relation between Na^+ and SO_4^{2-}. Cardrona River water is plotted as a (*); Arrow River water is plotted as a (+). Seawater concentration–dilution line is shown for reference

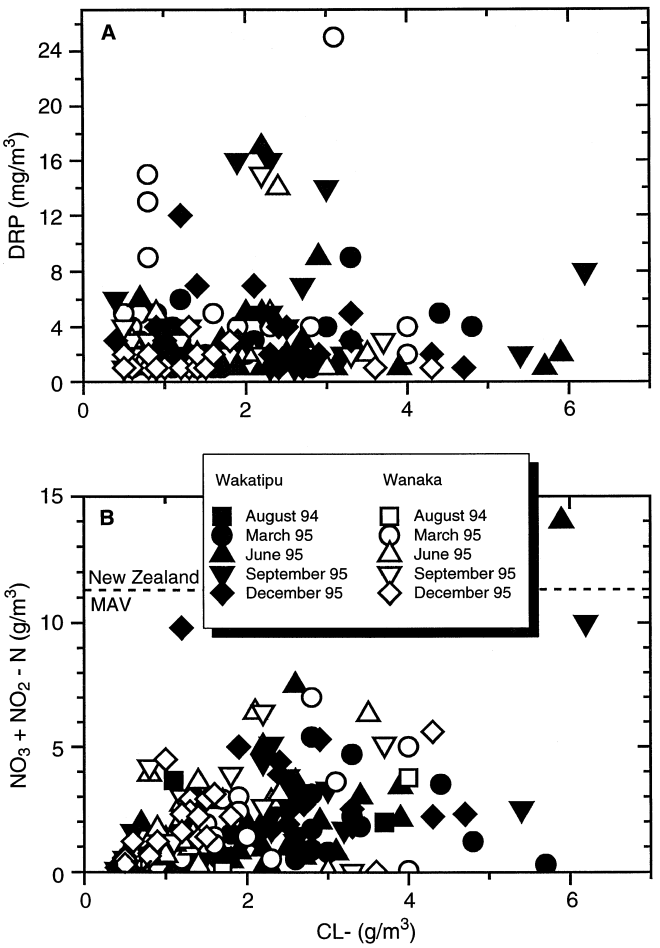

Fig. 9A, B Relation between nutrient concentrations and Cl^-. **A** Dissolved reactive phosphorus (DRP); **B** nitrate + nitrite-nitrogen (NNN). Cardrona River water is plotted as a (*) and Arrow River water is plotted as a (+) in *Figure 9B*; no DRP data are available for the rivers. One sample from each basin is not plotted because each has a Cl^- concentration greater than 7 g/m^3

groundwater is controlled by a relatively minor component of the bedrock. If calcite dissolution from the Otago Schist is controlling the chemical make-up of groundwater, then a highly soluble ubiquitous accessory mineral such as calcite can dominate the chemistry of groundwater throughout large portions of the alluvial aquifers in the Wanaka and Wakatipu basins, and essentially all of Central Otago where calcite-bearing Otago Schist clasts are an important component of the aquifers.

Although local sources of calcium carbonate are present either as outcrops of Tertiary-age limestone west of the study area (Turnbull et al. 1975) or as palaeolake marls in the Wakatipu basin, their areal extent

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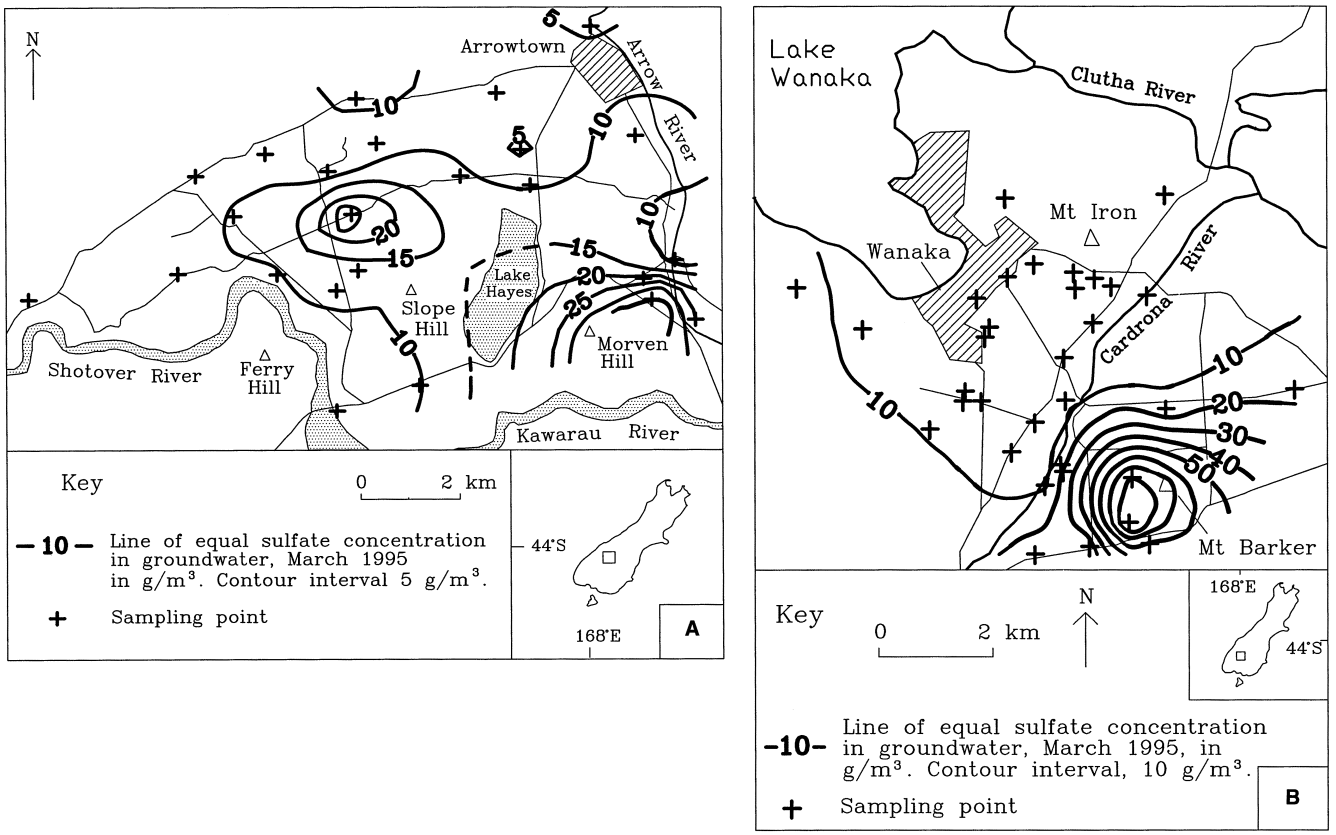

Fig. 10, B Distribution of SO_4^{2-} for **A** the Wakatipu basin and **B** the Wanaka basin, March 1995

and distribution is insufficient to account for the constant Ca^{2+}:HCO_3^- equivalent ratios throughout both basins. However, the distribution of higher HCO_3^- concentrations around Lake Hayes, shown in *Figure 11A*, may be due to the locally abundant Pleistocene-age marl sediments. In the Wanaka basin, even fewer limestone sources are known, even though the Ca^{2+}:HCO_3^- equivalent ratios of groundwater are also near 1:1. The higher HCO_3^- concentrations in the Wanaka basin are grouped near the mountainous fringes of the basin, where the schists crop out, as shown in *Figure 11B*. Lower concentrations of Ca^{2+} and HCO_3^- down gradient are probably caused by dilution by Cardrona River water and rainwater input to the aquifer.

The dissolution of anorthite (a calcium feldspar) could also produce a water that has 1:1 Ca^{2+}:HCO_3^- equivalent ratios. However, dissolution of anorthite would also produce silica as part of the weathering reaction. The few measurements of silica in groundwater in both basins indicate contents that are relatively low (on average, 11 g/m^3) and suggest that significant silicate weathering reactions are not taking place. In addition, anorthite is not part of the Otago Schist mineral assemblage.

Mast et al. (1990) shows that the chemical composition of surface water in the Loch Vale watershed, Rocky Mountain National Park, Colorado, USA, is controlled by the dissolution of calcite from the bedrock granite and metamorphic rocks, even though the calcite is present in only trace quantities. They show that the reactivity of the calcite is the most important reason for the dominance of calcium and bicarbonate in solution and that the importance of feldspar dissolution is minor. This study confirms the study of Mast et al. (1990) and extends the hypothesis that dissolution of trace amounts of calcite from bedrock can dominate the chemical composition of natural solutions to groundwater systems.

Source and Distribution of Na^+ and SO_4^{2-}

The occurrence of higher-sulphate waters associated with outcrops of schist suggests that local sulphide deposits may exist within the schist, and that the occurrence of relatively fresh basement rock near the surface controls the concentration of sulphate in the groundwater. Sulphide ore deposits are not uncommon within the Otago Schist (Turnbull and Forsyth 1988). The higher-sulphate water may be derived directly from fractured bedrock and can be distinguished from the high-bicarbonate waters that are derived from reworked basement (i.e., in alluvial aquifers). Evidence from tritium measurements of the higher-sulphate water indicates that it is older and derived from a source that is different from the high-bicarbonate waters (Rosen et al. 1997). Youngson (1995) shows that deep

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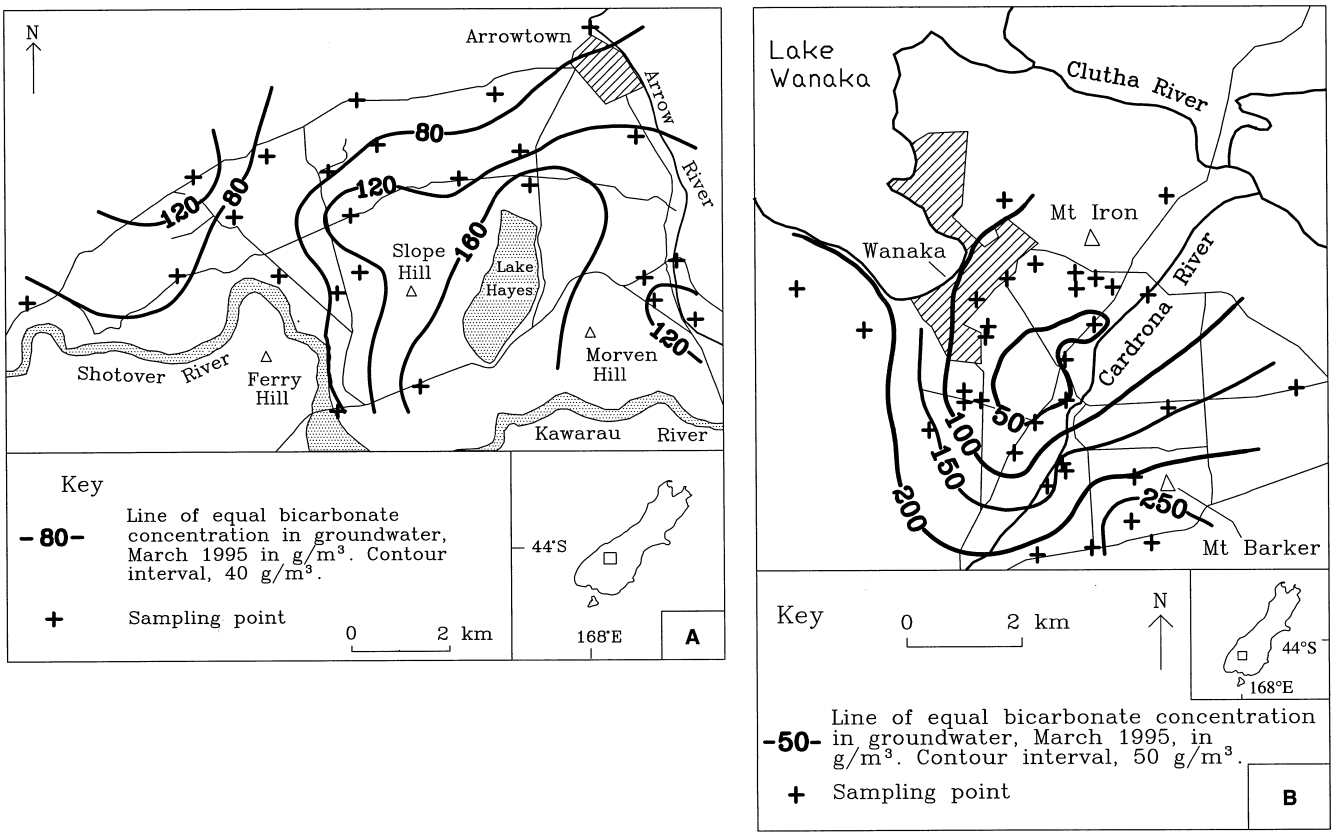

Fig. 11A, B Distribution of HCO_3^- for **A** the Wakatipu basin and **B** the Wanaka basin, March 1995

groundwater in some Central Otago groundwater systems has high-sulphate concentrations because no hydraulic outlet exists for this groundwater. He attributs the high-sulphate concentrations in the deep groundwater to dissolution of sulphide minerals during uplift of the sediments. In the Wanaka and Wakatipu basins, the high-sulphate groundwater is not necessarily associated with deep bores, but is associated with possible discharge areas of deep groundwater coming from the underlying schist.

The association of higher sodium with higher sulphate concentrations in the groundwater is puzzling. A significant portion of the sodium in groundwater is probably derived from marine aerosols and brought in by rain or snow. Evidence for this can be seen in the plot of Na^+ versus Cl^-, which follows the slope of the seawater evaporation–concentration line (*Fig. 5A*). However, the higher Na^+ samples in the Wanaka basin do not follow this trend, indicating another source for the sodium. The most likely source(s) of sodium in groundwater are the dissolution of feldspars or cation exchange within some clays. One possible scenario is that dissolution of sulphide minerals would create acid groundwater that would then attack feldspars and release Na^+ into solution. However, this reaction has not been documented in this area. As mentioned above, the average monomeric silica concentrations are low, indicating that the dissolution of silicates is not a dominant reaction.

Source and Distribution of K^+

Two sources of ions in groundwater are distinguished, based on Na^+ and K^+ concentrations (*Fig. 6*). In general, groundwater in the Wanaka basin has higher Na^+ and lower K^+ concentrations, and groundwater in the Wakatipu basin has higher K^+ and lower Na^+ concentrations, although at low concentrations groundwaters in both basins follow the same trend (*Fig. 6*). Statistically, little difference exists between the concentrations of K^+ in the two basins; in the Wanaka basin, the mean concentration is 1.2 ± 0.3 g/m^3 ($N = 116$), and in the Wakatipu Basin, the mean concentration is slightly higher at 1.5 ± 0.8 g/m^3 ($N = 120$). However, the much larger standard deviation in the Wakatipu data indicates a large range of K^+ concentrations and confirms the higher K^+ concentrations shown graphically. Higher K^+ concentrations in the Wakatipu basin also correspond to lower SO_4^{2-} concentrations (Rosen et al. 1997), indicating that the higher K^+ concentrations are not related to the same basement control as the higher SO_4^{2-} groundwater.

Given that both basins include gravel composed of essentially the same lithologies, and that the higher K^+ concentrations are unrelated to basement-controlled

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groundwater, the higher K^+ concentrations in the Wakatipu basin are an anomaly. Although it is possible that increased K^+ concentrations could be related to K-feldspar dissolution, there is no reason to suspect that significantly more K-feldspars occur in the Wakatipu basin than in the Wanaka basin. In fact, the Wanaka basin probably contains more K-feldspar, because it is underlain by the Torlesse terrane, which contains abundant K-feldspar in the protolith granitic sandstone, compared with the largely volcanoclastic sandstone origin of much of the Wakatipu catchment (I. Turnbull, pers. comm. 1996). Another alternative is that the higher K^+ concentrations are caused by anthropogenic sources, such as the spreading of K-rich fertilisers. The spreading of fertilisers may be more prevalent in the Wakatipu basin than in the Wanaka basin, because some of the land uses in Wakatipu include vineyards and orchards, whereas the predominant land use in the Wanaka basin is animal husbandry, and no significant horticultural areas exist there.

Types and Distribution of Nutrients

Concentrations of DRP, NH_4^+, TP, and TDP are low in both basins. DRP concentrations average 3 mg/m^3 in both basins (*Fig. 9A*) and show no discernible spatial distribution. The only nutrient measured of significance in groundwater of either basin is nitrate (*Fig. 9B*). Nitrate concentrations are variable, but are excessively high in samples from a few wells in both basins. Total nitrogen (TN) concentrations reflect the amount of nitrate detected, and ammonium (NH_4^+) concentrations appear to have an antithetic relationship with nitrate concentrations in the Wakatipu basin. These conditions probably reflect the oxidation state of the water, because oxidised water is likely to contain nitrate as the stable form of nitrogen, and water with low dissolved-oxygen concentrations has higher NH_4^+ concentrations.

Specific Aspects of Land Use and Human Impact

Anthropogenic sources of ions in groundwater, particularly in the Wanaka basin, are indicated by the fact that nitrate concentrations consistently increase with Cl^- (*Fig. 9B*). Nitrate concentrations are generally below New Zealand's maximum acceptable value of 50 g/m^3 NO_3^- in both basins, but no natural sources of NO_3^- are known that could raise the concentration of NO_3^- to those measured. Background concentrations of NO_3^- are approximately 0.40 g/m^3 NO_3^-, and the average concentration for both the Wanaka and Wakatipu basins is about 8 g/m^3 NO_3^-, with a maximum concentration of 186 g/m^3 NO_3 from one bore in the Wanaka basin. Given that both basins are dominated by rural land uses, such as sheep, deer, and cattle farming, as well as some orchards and vineyards, elevated concentrations of NO_3^- from animal wastes and fertiliser are not surprising.

Conclusions

The Wakatipu and Wanaka basins are both underlain by green and grey schist of the Otago Schist and the alluvial aquifers in these basins are derived predominantly from this material. Although calcite is only a minor to trace accessory mineral in these rocks, the dissolution of calcite dominates the chemical composition of the alluvial aquifers in both basins. Ca^{2+} and HCO_3^- account for >80% of ions in groundwater, and they occur in a 1:1 equivalent ratio. Therefore, minor and trace accessory minerals should always be considered when assessing the impact of geology on the chemical compositions of groundwater systems.

Where the schists are near the surface, groundwater contains more Na^+ and SO_4^{2-}. These areas may represent deeper and/or older groundwater associated with the dissolution of sulphides and Na-feldspars in the basement rocks. Anomalously high K^+ concentrations in the Wakatipu basin cannot be linked to groundwater-rock interaction and may be the result of increased K-rich fertiliser use needed for horticultural land uses that do not exist in the Wanaka basin. A moderate correlation between Cl^- and NO_3^- concentrations in the Wanaka basin suggests that elevated concentrations of these ions are caused by agricultural practices in the basin.

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Appendix

Table A1 Selected chemical analyses of groundwater and the Arrow River, Wakatipu basin

Borehole ID	Date	pH	Sp. Cond., mS/m	Temp., °C	Concentration, g/m^3													
					Na^+	K^+	Ca^{2+}	Mg^{2+}	HCO^{3-}	Cl^-	SO_4^{2-}	SiO_2	NO_3-NO_2-N	NH_4^+-N	TN-N	DRP	TP	TDP
F410003	21-Jun-95	6.27	11	9.7	3.1	0.8	18	1.9	58	1.3	9.6	*	0.67	0.009	0.82	0.002	<0.001	<0.001
	26-Sep-95	6.39	14.2	8.3	3.1	0.5	15	1.7	42	2	9.9	*	1.5	0.029	1.6	0.003	<0.005	<0.003
	8-Dec-95	5.91	14.45	9.3	3.5	0.8	17.7	2	53	1.6	10	*	0.61	0.02	1.1	0.002	<0.005	<0.003
F410009	20-Jun-95	6.8	11	*	3.4	2.2	16	1.7	42	1.7	11	*	2.8	0.011	3.1	0.003	0.007	0.003
	26-Sep-95	6.33	19.4	7.4	4.3	2.2	19	2.5	39	2.7	20	*	3.2	0.027	3.6	0.007	0.007	0.006
	7-Dec-95	6	16.71	12.2	4.4	2.7	19.5	2.6	52	2.5	12	*	2.4	0.012	3	0.004	0.006	0.005
F410023	2-Mar-95	6.53	17	10.8	2.8	1.1	23	2.5	71	1.4	13	*	0.4	<0.003	1.4	0.001	<0.001	<0.001
	20-Jun-95	6.4	14	9.9	2.9	1.2	25	2.6	75	1	13	*	1.3	0.022	1.5	0.003	0.002	0.001
	26-Sep-95	6.3	21.8	6.6	3.4	0.6	25	3	76	1.2	12	*	1.5	<0.006	1.4	0.003	<0.005	0.003
	7-Dec-95	6.01	20.7	10.9	3.3	0.9	24.9	3.2	85	1.3	11	*	1.6	0.015	1.7	0.002	<0.005	<0.003
F410028	3-Mar-95	7.21	27	11.6	5.2	1.1	26	1.1	83	1	5.9	*	0.11	0.012	1.3	0.003	0.12	0.003
	20-Jun-95	6.59	5	8.2	2.1	0.4	7.4	0.5	24	0.8	4.4	*	0.3	0.011	0.46	0.002	0.003	<0.001
	26-Sep-95	5.84	5.35	5.8	1.8	0.4	5.3	0.4	18	0.4	2.3	*	0.1	<0.006	0.4	0.006	0.034	0.01
	8-Dec-95	5.3	5.39	11.1	2.2	0.3	6.2	0.5	22	0.4	2.9	*	0.18	0.012	0.31	0.003	<0.005	<0.003
F410036	21-Jun-95	8.6	10	8.6	2.5	1.9	17	0.5	50	1	7.3	*	1.3	0.01	1.5	0.003	0.001	<0.001
	26-Sep-95	5.86	9.3	6.8	2.2	2.6	9	0.5	21	0.6	7.6	*	1.6	0.025	2	0.003	<0.005	<0.003
	8-Dec-95	5.82	10.99	12	2.4	1.8	14.3	0.5	37	0.9	6.3	*	1.5	0.012	2.1	0.004	0.009	0.005
F410042	20-Jun-95	6.08	19	7.3	4.6	3	29	5.2	93	2.2	11	*	5	0.016	5.4	0.001	0.003	0.002
	27-Sep-95	6.7	22.7	9.6	4.9	3.2	29	5.3	97	2.3	9.9	*	5.1	<0.006	5.2	0.001	0.005	<0.003
	8-Dec-95	6.97	19.6	12.2	4.8	2.9	29.2	5.3	95	2.4	11	*	4.4	0.009	4.5	0.001	<0.005	<0.003
F410051	3-Mar-95	6.31	34.7	15.2	4.6	1.4	62	6.2	188	2.8	34	*	0.87	<0.003	0.99	0.001	<0.001	0.002
	20-Jun-95	6.91	31	7.7	4.4	1.5	59	6	179	1.9	32	*	0.8	0.014	0.92	0.001	<0.001	<0.001
	26-Sep-95	6.55	31.4	10.3	4.1	1.2	52	5.8	160	1.7	29	*	0.69	0.01	0.69	0.002	<0.005	<0.003
	8-Dec-95	6.89	29.5	14	4.4	1.5	56.8	6.8	168	2.3	27	*	1.7	0.023	1.8	0.002	<0.005	<0.003
F410053	20-Jun-95	7.33	19	6.6	4.7	1.7	36	2.5	131	0.9	8	*	0.032	0.01	<0.080	0.003	0.008	0.003
	27-Sep-95	7.08	23.6	8	5.1	1.5	37	2.7	131	0.9	7.9	*	0.015	<0.006	<0.08	0.002	0.005	0.003
	7-Dec-95	6.52	22.5	17	5	2.1	37.6	2.6	132	1	8.7	*	0.012	0.007	<0.08	0.003	0.006	0.004
F410059	2-Mar-95	7.32	44	11.7	5.1	2.2	63	4.3	215	4.4	9.8	*	3.5	0.003	3.5	0.005	0.009	0.007
	20-Jun-95	6.92	33	7	5.3	2.2	67	4.1	214	3.4	8.6	*	3	0.021	3.3	0.002	0.013	0.013
	26-Sep-95	6.54	36.3	7.2	5.4	2	61	4.1	200	3	7.9	*	3.3	0.02	3.5	0.014	0.036	0.014
	7-Dec-95	6.7	37.1	16	5.6	2.2	66.1	4.4	215	3.3	9	*	2.5	<0.006	2.7	0.003	0.021	0.011
F410065	3-Mar-95	7.21	27	11.6	4.3	1.3	41	4.6	126	3.4	14	*	1.8	<0.003	4	<0.001	<0.001	<0.001
	21-Jun-95	6.51	25	10.3	5.4	1.9	38	5.4	120	3.6	17	*	*	*	5.7	*	0.006	*
	27-Sep-95	6.48	22.4	9.6	3.8	0.8	31	4.6	96	2.2	13	*	4.4	<0.006	4.3	0.005	<0.005	0.005
	7-Dec-95	6.7	30.3	11.3	4.3	1.9	40.1	5.2	120	2.9	14	*	5.3	0.01	4.9	0.002	<0.005	<0.003

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Table A1 Continued

Borehole ID	Date	pH	Sp. Cond., mS/m	Temp., °C	Concentration, g/m^3													
					Na^+	K^+	Ca^{2+}	Mg^{2+}	HCO^{3-}	Cl^-	SO_4^{2-}	SiO_2	NO_3-NO_2-N	NH_4^+-N	TN-N	DRP	TP	TDP
F410075	3-Mar-95	7.38	25.6	13.5	4.1	1.6	39	6	119	2.8	24	*	3.1	0.007	3.8	0.001	<0.001	<0.001
	21-Jun-95	6.71	24	10.4	4	1.7	40	6.2	125	2.5	24	*	2.7	0.011	3.2	0.002	<0.001	<0.001
	26-Sep-95	6.19	58.2	9.9	4.1	1.4	41	6.5	126	2.6	25	*	3	0.037	3.2	0.002	<0.005	<0.003
	7-Dec-95	6.06	27.1	11	4.4	1.7	41.7	6.9	129	2.7	25	*	2.7	0.012	2.9	0.001	<0.005	<0.003
F410084	21-Jun-95	7.21	21	6.6	3.3	1.1	39	4.1	128	2	9.1	*	1.9	0.021	2.1	0.005	0.01	0.007
	27-Sep-95	6.67	27.4	8.4	3.9	1.3	43	4.5	141	2.3	11	*	1.7	<0.006	1.8	0.016	0.034	0.015
	7-Dec-95	6.5	28.9	12.1	3.8	1.5	41.8	4.2	140	2.5	8.2	*	1.9	0.012	2	0.002	0.006	0.005
F10085	3-Mar-95	5.79	22.7	13.2	3.4	1.1	39	3.3	131	1.8	7.9	*	1.5	<0.003	1.6	<0.001	<0.001	0.011
	21-Jun-95	6.68	20	8.2	2.8	1.1	38	3.1	127	1.1	7.5	*	1.1	0.011	1.4	0.001	0.002	0.001
	26-Sep-95	6.31	26.4	10.9	3.1	0.8	40	3.4	129	1.3	8.3	*	1.7	0.023	1.9	0.002	<0.005	<0.003
	7-Dec-95	6.33	25.5	11.6	3.2	1.1	39.9	3.5	132	1.5	9.2	*	1.2	0.022	2	0.001	<0.005	<0.003
F410104	11-Aug-94	7.6	32	11.1	4.9	1.5	53.5	5.4	185.6	1.4	8.9	17.8	0.05	*	*	*	*	*
	2-Mar-95	6.39	30.8	13	4.5	1.3	54	5.6	199	1.2	9.2	*	0.13	0.28	0.41	0.006	0.034	0.014
	19-Jun-95	6.72	28	10.8	4.7	1.3	54	5.6	199	1.1	9	*	0.032	0.29	0.36	0.001	0.023	<0.001
	26-Sep-95	7.21	39	11	5.2	1.2	51	5.7	196	1	8.2	*	0.007	0.31	0.29	0.003	0.025	0.004
	7-Dec-95	6.46	32.3	10.9	4.9	1.3	54.1	6.2	199	1.3	9.3	*	0.084	0.3	0.29	0.002	0.021	0.003
F410111	21-Jun-95	6.6	12	7.7	4.1	1.4	17	2.3	44	2.6	8.7	*	3.6	0.012	4.2	0.002	0.003	0.002
	26-Sep-95	5.98	13.5	9.1	4.2	1.2	16	2.4	44	2.5	8.5	*	3.8	0.015	3.9	0.004	<0.005	0.003
	7-Dec-95	6.75	13.2	10	4.4	1.5	18.3	2.5	51	2.4	8.7	*	3.9	0.01	3.7	0.004	0.007	<0.003
F410115	11-Aug-94	6.9	20	9.3	4	1.4	30.2	3.7	80.9	2.6	9	10.6	1.407	*	*	*	*	*
	2-Mar-95	5.71	18.9	11.5	3.4	1.2	28	3.4	98	2.6	9	*	0.51	0.078	1.3	<0.001	<0.001	<0.001
	20-Jun-95	6.78	17	8.3	3.5	1.2	27	3.3	101	2.2	8.9	*	0.91	0.078	1	0.001	0.009	<0.001
	27-Sep-95	6.77	19.7	8.8	3.8	1.4	27	3.6	98	2.6	8.8	*	1.2	0.078	1.3	0.001	0.029	<0.003
	7-Dec-95	6.64	17.2	10.2	3.8	1.3	26.9	3.4	93	2.7	6.6	*	0.8	0.2	0.99	0.002	0.033	<0.003
F410118	11-Aug-94	6.8	30	11.1	5.5	1.5	41	7.7	106.8	3.7	43	9.4	1.97	*	*	*	*	*
	3-Mar-95	6.22	30.2	12.5	5.5	1.4	42	8.3	112	4.8	53	*	1.2	0.006	1.3	0.004	0.004	0.022
	21-Jun-95	6.91	24	10.4	5.3	1.3	37	7.2	101	2.5	45	*	0.95	0.008	1.1	0.002	<0.001	<0.001
	26-Sep-95	6.22	34.4	9.9	6.8	1.2	38	7.8	110	3.2	44	*	1.7	0.029	1.7	0.002	<0.005	<0.003
	7-Dec-95	6.21	31.5	9.6	7.3	1.4	44.3	8.8	116	4.3	64	*	2.2	0.012	2.5	0.002	<0.005	<0.003
F410122	11-Aug-94	8.1	13	8.6	1.8	0.7	22.4	1.3	69.2	0.6	6.8	6.4	0.059	*	*	*	*	*
	2-Mar-95	6.61	12.9	12.2	1.6	0.6	23	1.3	74	0.6	7	*	0.86	<0.003	<0.08	0.005	<0.001	0.041
	20-Jun-95	6.5	11	6	1.6	0.7	22	1.3	71	<0.6	7	*	0.067	0.008	0.081	0.001	0.002	0.001
	26-Sep-95	7.08	13.7	8.1	1.5	0.5	22	1.4	73	0.5	6.9	*	0.081	0.01	<0.08	0.002	<0.005	<0.003
	7-Dec-95	6.88	14.1	12.3	1.8	0.6	22.9	1.4	75	0.5	7.1	*	0.4	0.016	0.12	0.002	<0.005	0.003
Arrow River	3-Mar-95	*	*	*	1.5	0.6	19	1.9	68	0.4	3.8	*	0.012	<0.003	<0.08	<0.001	*	<0.001

* Not analyzed

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Table A2 Selected chemical analyses of groundwater and the Cardrona River, Wanaka basin

Borehole ID	Date	pH	Sp. Cond., mS/m	Temp., °C	Concentration, g/m^3													
					Na^+	K^+	Ca^{2+}	Mg^{2+}	HCO^{3-}	Cl^-	SO_4^{2-}	SiO_2	NO_3-NO_2-N	NH_4^+-N	TN-N	DRP	TP	TDP
F400001	28-Feb-95	6.99	12	11.1	3.1	1.1	18	2.1	72	1.1	4.4	*	0.74	0.013	0.73	0.002	0.003	0.001
	20-Jun-95	7	10	9.1	2.8	1.2	17	2.1	66	0.8	4.4	*	0.58	0.008	0.7	0.001	<0.001	0.001
	26-Sep-95	6.9	11	10.5	3	0.8	18	2.3	67	0.8	4.3	*	0.62	0.01	0.59	0.002	<0.005	0.005
	7-Dec-95	6.5	10.9	15.6	3.1	1	18	2.2	66	0.6	4.4	*	0.64	0.014	0.7	0.001	<0.005	<0.003
F400003	28-Feb-95	8.16	20	13.4	3	1.1	31	2.1	108	1.1	4.3	*	0.88	0.007	0.92	0.003	0.006	0.002
	20-Jun-95	8	16	10.5	2.8	1.2	30	2.2	105	0.8	4	*	0.73	0.01	0.79	0.001	0.003	<0.001
	26-Sep-95	8.06	16	10	3.1	1	29	2.3	102	0.7	4.2	*	0.57	0.008	0.56	0.002	<0.005	0.003
	7-Dec-95	7.6	16.4	13.7	3.1	1	30	2.2	103	0.8	4.4	*	0.74	0.011	0.74	0.001	<0.005	<0.003
F400022	1-Mar-95	6.79	12.1	11.6	3	1.1	19	2.2	68	0.9	4.6	*	0.86	0.006	0.82	0.003	<0.001	0.023
	19-Jun-95	7.1	11	10.2	2.8	1.1	18	2.1	67	0.6	4.2	*	0.58	0.009	0.64	0.001	<0.001	0.001
	27-Sep-95	6.87	11.56	10.1	3	0.7	18	2.2	65	0.6	4.1	*	0.56	<0.006	0.52	0.002	<0.005	0.003
	7-Dec-95	6.4	12.1	10.8	3.4	1.1	18.6	2.2	66	0.6	4.6	*	1.2	0.008	1.2	0.001	<0.005	<0.003
F400027	21-Jun-95	7.63	29.9	8.5	4.7	1.5	55	3.5	177	0.8	7	*	3.9	0.009	4.9	0.001	<0.001	0.002
	26-Sep-95	7.71	29.9	8.9	4.6	1.2	55	3.6	173	0.8	6.8	*	4.2	0.006	4.4	0.003	<0.005	<0.003
	7-Dec-95	7.35	32.8	13.8	5	1.5	56.3	3.6	177	1	8.1	*	4.5	0.014	4.8	0.001	<0.005	<0.003
F400033	20-Jun-95	6.8	9	9.1	2.9	1.4	14	1.5	54	<0.6	4.2	*	0.37	0.011	0.56	0.003	0.003	0.003
	26-Sep-95	6.75	9.6	9.8	2.9	1.5	15	1.6	55	0.5	3.9	*	0.52	<0.006	0.5	0.004	<0.005	0.003
	8-Dec-95	5.64	9.4	11.6	3.4	1.3	15.9	1.7	56	0.5	4.3	*	0.49	0.007	0.52	0.002	<0.005	<0.003
F400052	1-Mar-95	7.2	44	12.7	10	1.6	59	12	229	3.1	21	*	3.6	0.025	3.9	0.025	0.022	0.022
	21-Jun-95	8	38	12	11	1.6	55	13	246	2.3	23	*	2.8	0.011	3	0.005	0.028	0.019
	26-Sep-95	7.15	40	10.9	11.3	2.2	62	13.5	247	2.2	24	*	2.6	<0.006	2.5	0.015	0.022	0.017
F400056	1-Mar-95	7.37	55	12.2	20	1.7	90	21	305	4	97	*	0.051	0.028	<0.08	0.004	0.001	0.005
	21-Jun-95	7.8	54	12.2	20	1.7	87	21	307	3	94	*	0.031	0.023	<0.08	0.001	0.001	0.003
	26-Sep-95	7.31	56	11.9	19.9	1.6	87	22	307	3.3	94	*	0.028	0.021	<0.08	0.002	<0.005	<0.003
	7-Dec-95	7.2	59.7	12.3	19.7	1.8	87.2	21	309	3.6	92	*	0.008	0.029	<0.08	0.001	0.005	0.003
F400057	1-Mar-95	7.41	9.1	13	15	2.1	130	21	202	32	82	*	42	0.019	41	0.003	0.001	0.008
F400059	1-Mar-95	7.77	3.8	12	7.2	1.2	50	7.1	174	1.7	17	*	2.9	0.007	2.7	0.001	0.001	0.007
	20-Jun-95	7.9	27	11.8	7.3	1.2	50	7.2	174	1.3	17	*	0.94	0.013	2.6	0.001	0.005	0.002
	26-Sep-95	7.6	29	11.7	7.2	0.9	47	7.6	172	1.3	17	*	2.4	<0.006	2.4	0.002	<0.005	<0.003
	7-Dec-95	7.3	29.8	12	7.6	1.1	46.7	7.2	172	1.3	17	*	2.4	0.015	2.5	0.001	<0.005	0.004
F400061	21-Jun-95	7.5	23	12.3	6.7	1.2	37	6.2	137	1.2	14	*	2.1	0.01	2.4	0.001	0.005	0.004
	26-Sep-95	7	23	12	7.1	1	35	6.2	130	1.3	13	*	2.3	0.006	2.3	0.002	<0.005	<0.003
	7-Dec-95	6.6	24.2	12.8	7	1.2	37.1	6.2	135	1.2	14	*	2.3	0.012	2.3	0.001	<0.005	0.003
F400068	1-Mar-95	7.66	39.3	15.2	4.3	1.3	78	6.3	256	1.9	6.4	*	3	0.007	3.1	0.003	0.001	0.005
	19-Jun-95	7.5	37	10.7	4.4	1.4	82	6.4	264	1.2	6.4	*	2.7	0.011	3.1	0.002	0.005	0.003
	26-Sep-95	7.35	42.3	12	4.9	1.1	80	7.1	273	1.2	6.7	*	3	0.014	2.9	0.003	0.006	0.004
	7-Dec-95	7.12	45.6	16.8	4.9	1.4	81.9	6.8	279	1.2	7.1	*	1.6	0.017	2.2	0.001	0.007	<0.003

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Table A2 Continued

Borehole ID	Date	pH	Sp. Cond., mS/m	Temp., °C	Concentration, g/m^3													
					Na^+	K^+	Ca^{2+}	Mg^{2+}	HCO^{3-}	Cl^-	SO_4^{2-}	SiO_2	NO_3-NO_2-N	NH_4^+-N	TN-N	DRP	TP	TDP
F400073	1-Mar-95	6.44	34.5	14.8	4.7	1.5	68	4.3	218	1.6	12	*	1.4	0.006	1.3	0.002	<0.001	<0.001
	19-Jun-95	7.5	31	12	4.5	1.6	69	4.2	221	1.1	12	*	1.1	0.011	1.2	0.002	<0.001	<0.001
	26-Sep-95	7.35	34.8	10.8	4.4	1.2	66	4.5	219	1.1	11	*	1.2	<0.006	1.2	0.002	<0.005	<0.003
	7-Dec-95	6.8	36.7	13.9	5	1.6	66.6	4.5	216	1.4	11	*	1.3	0.009	1.4	0.001	<0.005	0.003
F400081	28-Feb-95	7.12	12	12.8	3.7	0.6	14	1.1	55	2.3	2	*	0.5	0.015	0.51	0.004	0.004	0.005
	21-Jun-95	7.1	8	11.2	2.6	0.6	13	1	51	1.4	1.2	*	0.26	0.009	0.24	0.002	0.005	0.005
F400104	10-Aug-94	7.57	61.8	11.4	9.8	1.3	98.3	15.6	271.8	1.7	56.4	13.4	0.036	*	*	*	*	*
F400107	10-Aug-94	6.6	11	10.1	2.8	1.2	15.4	2	57	0.6	4.4	9.3	0.259	*	*	*	*	*
	28-Feb-95	7.07	10.15	12.5	2.7	1.2	15	1.7	58	0.7	3.8	*	0.27	0.015	0.28	0.003	0.002	0.016
	21-Jun-95	6.78	*	10.2	2.6	1.2	15	1.8	57	<0.6	3.9	*	0.47	0.007	0.49	0.002	0.001	0.001
	27-Sep-95	6.91	9.63	10.5	2.5	1.4	14	1.8	57	0.5	3.6	*	0.28	<0.006	0.28	0.002	<0.005	<0.003
	7-Dec-95	6.5	11.7	12.3	3	1.1	15.1	1.9	58	0.5	3.9	*	0.26	0.008	0.29	0.002	<0.005	<0.003
F400115	10-Aug-94	7.6	43	10.2	13.8	2.4	91.5	7.2	212.3	4	28.2	15.8	3.764	*	*	*	*	*
	1-Mar-95	6.1	41.3	14.2	14	1.7	59	12	222	4	25	*	5	0.009	5	0.002	0.001	0.002
	21-Jun-95	6.78	*	10.4	14	1.7	59	12	221	3.5	25	*	6.3	0.007	5.6	0.002	0.003	0.002
	27-Sep-95	6.79	42.1	11.1	13.5	1.7	60	12.6	225	3.7	25	*	5.1	<0.006	4.9	0.003	<0.005	0.003
	7-Dec-95	6.44	14	14.4	13.5	1.6	61.7	12.5	226	4.3	25	*	5.6	0.007	5.5	0.001	<0.005	<0.003
F400121	10-Aug-94	7.8	10	3.7	2.7	1.2	15.9	1.8	63.1	0.5	4	8.4	0.138	*	*	*	*	*
	28-Feb-95	6.28	8.44	12.8	2.4	1.1	13	1.4	50	0.6	3.2	*	0.32	0.004	0.42	0.003	0.011	0.004
	20-Jun-95	7.2	9	5.5	2.4	1.2	15	1.7	57	<0.6	3.6	*	0.049	0.007	0.34	0.002	0.002	0.001
	26-Sep-95	7.3	10.19	7.5	2.5	2	16	1.7	61	0.5	3.8	*	0.25	<0.006	0.25	0.001	<0.005	0.003
	7-Dec-95	6.62	10.09	14.7	2.6	1.1	15.2	1.8	55	0.5	4.1	*	0.3	0.009	0.29	0.001	<0.005	<0.003
F400124	10-Aug-94	7.5	32	6.5	8.3	4.6	52	4.6	178.4	1.5	10.1	15.1	1.055	*	*	*	*	*
	28-Feb-95	6.78	27.7	13.2	5.5	1.4	48	4	163	1.6	10	*	1.1	0.006	1.3	0.001	0.001	0.003
	8-Dec-95	6.76	26.7	12.8	5.4	1.3	49.2	4.4	169	1.5	11	*	1.4	0.008	1.4	0.001	<0.005	<0.003
F400128	1-Mar-95	6.58	36.2	12.5	11	1.3	50	10	175	2.8	23	*	7	0.006	7.4	0.004	0.001	0.002
	21-Jun-95	7.15	33.7	10.9	11	1.3	46	11	174	2.1	24	*	6.4	0.014	6.5	0.002	0.005	0.003
	26-Sep-95	7	34	9.2	10.9	1.1	48	11.1	173	2.2	26	*	6.4	<0.006	6.4	0.002	<0.005	<0.003
	7-Dec-95	6.8	38	11.9	11.3	1.4	56.1	12.1	214	1.6	24	*	3.1	0.014	3	0.002	0.005	0.004
Cardrona River	10-Aug-94	9.39	8.9	5.2	2.4	1	13.2	1.5	47.3	0.7	4.1	8.4	0.049	*	*	*	*	*

* Not analyzed

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