

HYDROCHEMICAL VARIATION IN A WATER-TABLE AQUIFER BENEATH GRAZED PASTURELAND

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ABSTRACT

Land-use and geohydrological factors strongly influence the chemical quality of a water-table aquifer. The composition of shallow groundwater located between Ashburton and Rakaia Rivers on the Canterbury Plains (New Zealand) is principally governed by seepage from local rivers and by drainage from irrigated and non-irrigated pastureland.

The Ashburton-Rakaia aquifer has been divided into four chemical zones on the basis of the absolute concentrations and relative proportions of: Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} , HCO_3^- and $\text{NO}_3\text{-N}$. Zone (1) lies in regions of recharge from rivers; zone (2) is located beneath non-irrigated pasture near the coast; zone (3) is beneath non-irrigated pasture near the inland foothills; and zone (4) lies beneath irrigated pasture.

Within zones (2) and (4) spatial differences in major ion concentrations are principally related to depth below the water table. Ca^{2+} and HCO_3^- concentrations increase and Na^+ , Cl^- and $\text{NO}_3\text{-N}$ concentrations decrease with depth below the water table. Ionic concentrations within zones (1) and (3) are more uniform because each zone is almost exclusively recharged from a single source.

Seasonal influx of drainage results in fluctuations in the composition of shallow groundwater. Concentrations of $\text{NO}_3\text{-N}$, Cl^- , SO_4^{2-} , Na^+ , Mg^{2+} and K^+ increase during winter in groundwater beneath non-irrigated pasture. Deep wells (>20–30 m) exhibit no recognisable seasonal concentration trends.

INTRODUCTION

Knowledge of the spatial and temporal distribution of chemical constituents in a water-table aquifer is valuable for understanding the relationships between land use and groundwater quality and for predicting the impact of future changes in land use. Non-point contamination from an agricultural source has been shown to affect the areal and vertical (Saffigna and Keeney, 1977) and areal and temporal (Rajagopal, 1978; Burden, 1980) distributions of nitrate-N and chloride in groundwater. Spalding and Exner (1980) found that the spatial and temporal variation in concentration of reactive and non-reactive solutes in a shallow groundwater system reflected up-gradient land use and soil type.

The purposes of this study were to investigate the spatial and temporal pattern of major ion chemistry of the Ashburton-Rakaia water-table

aquifer and to determine the relationships between groundwater composition and geohydrological and land use factors.

STUDY AREA

The investigated area occupies 1350 km² between Ashburton and Rakaia Rivers on the Canterbury Plains (Fig. 1). The plains consist of coalesced glacial outwash and postglacial alluvial fans deposited during climatic fluctuations of the Quaternary (Wilson, 1973). The gravels are up to 400 m thick in the central plains area, but this thickness decreases rapidly toward the Alps (Suggate, 1973). In the Ashburton-Rakaia region, depth to water table is generally in the range 10 to 30 m, but increases to about 90 m in the north-west. Seasonal water table fluctuations normally range from 1 to 8 m, but are as large as 30 m in some inland wells. Groundwater moves south-east from the foothills of the Southern Alps toward discharge areas beyond the coastline (Scott, 1980).

Input components of a water balance for Ashburton-Rakaia groundwater include seepage from local rivers and drainage of precipitation, irrigation and stock-race water. Mean annual flow in the Rakaia is 200 m³/s of which about 15 m³/s recharges groundwater downstream of the State highway bridge. Ashburton River is effluent inland of Ashburton township, but receives groundwater in coastal reaches. Net mean annual recharge from the river is only about 1 m³/s (Scott *et al.*, in prep.). Annual rainfall ranges from about 600 mm at the coast up to 1100 mm on the foothills of the Alps and contributes about 10 m³/s to groundwater (Walsh and Scarf, 1980). Approximately 14,000 ha of the Ashburton-Lyndhurst scheme is border-dyke irrigated. Deep percolation from the irrigated pastures contributes a further 3 m³/s to groundwater. Recharge by leakage from stock races amounts to a further 4 m³/s (Scott *et al.*, in prep.). Total recharge to groundwater from all known sources amounts to approximately 33 m³/s. However, runoff from the foothills and drainage from spray-irrigated land (10,000 ha) make a further unknown contribution to groundwater.

The soils of the area are derived from accumulations of alluvium and loess and are typically free-draining and shallow (average 30 cm). Water holding capacities range from about 45-85 mm (Ministry of Works and Development, unpublished data).

Intensive livestock grazing is the predominant land use in the Ashburton-Rakaia region. The existing Ashburton-Lyndhurst border-dyke irrigation scheme encompasses 25,900 ha of pasture (Fig. 1). Part of the proposed Lower Rakaia scheme is already spray-irrigated from groundwater and eventually about half the area of the proposed scheme will be irrigated in this way (Maidment *et al.*, 1980).

MATERIALS AND METHODS

The experimental program involved sampling Ashburton and Rakaia Rivers and a total of 26 wells (Fig. 1). Water from 22 domestic, three irrigation and one industrial well was sampled at approximately monthly intervals from July 1978 to May 1979. Details of well locations and

depths are summarised in Table 1. All wells were in regular use throughout the sampling program except for the irrigation wells which were in operation only from October 1978 to March 1979. Sampling was preceded by prolonged pumping (>10 mins) to clear pressure tanks and irrigation lines. Pumping was continued until temperature stability indicated a true groundwater sample was obtained. Ashburton and Rakaia

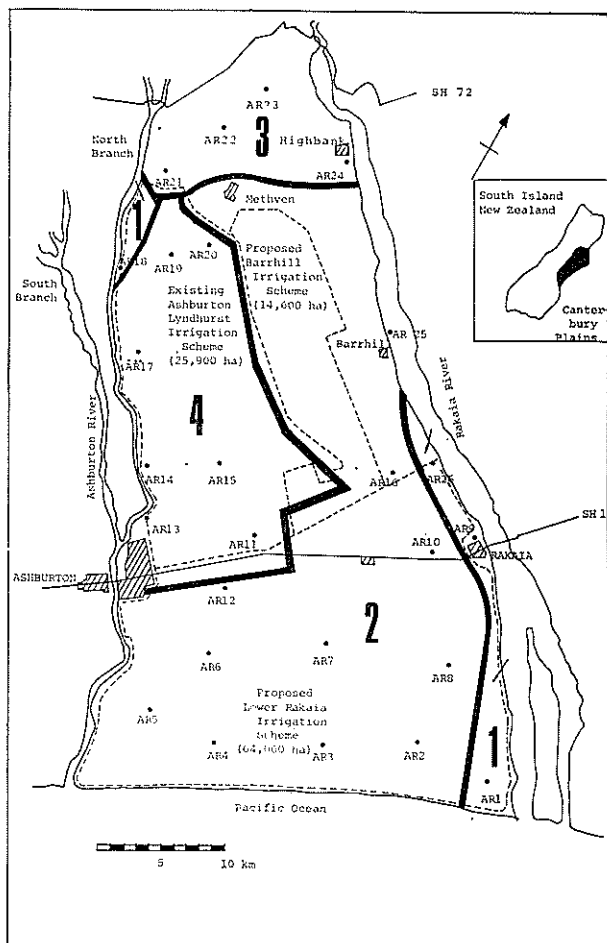


FIG. 1.—Map of the Ashburton-Rakaia region of the Canterbury Plains showing the positions of existing and proposed irrigation schemes, approximate boundaries of the four chemical zones, and locations of the observation wells. The chemical characteristics of each of the chemical zones are described in the text. The arrows indicate reaches over which river losses occur.

TABLE 1—Physical details of Ashburton-Rakaia wells. Depth below water table computed from summer 1974-1975 piezometric data (Ministry of Works and Development, unpublished data) and from local knowledge for wells AR21 to AR24.

Well No.	Map Reference	Total Well Depth (m)	Depth Below Water Table (m)
AR1	S93:564161	12.8	6
AR2	S93:493152	39.9	20
AR3	S92:399083	67.7	42
AR4	S92:325025	18.3	6
AR5	S92:273012	13.2	6
AR6	S92:299106	26.6	17
AR7	S92:368147	48.1	8
AR8	S93:501217	31.1	15
AR9	S93:458299	—	—
AR10	S92:427274	61.0	31
AR11	S92:297203	—	—
AR12	S92:268153	105.0	70
AR13	S92:202145	—	—
AR14	S92:193199	—	—
AR15	S92:250245	72.0	27
AR16	S82:384316	75.0	40
AR17	S92:132282	18.3	10
AR18	S82:088318	—	—
AR19	S82:123362	12.0	2
AR20	S82:123401	18.3	3
AR21	S82:061425	4.2	2
AR22	S82:056478	18.3	13
AR23	S82:085498	6.0	4
AR24	S82:208516	8.7	7
AR25	S82:294417	—	—
AR26	S82:359362	30.0	15

Rivers were sampled at their main channels on one occasion. The sample bottle was held at a depth of about 50 cm for approximately five minutes.

Water temperature was measured at the time of sampling with a mercury-in-glass thermometer to an accuracy of $\pm 0.2^\circ\text{C}$. Samples were taken in acid-cleaned polyethylene screwtop bottles. Sample bottles were completely filled and then refrigerated within 24 hours of collection. Cation analyses were made on a Varian Techtron AA100 atomic absorption spectrophotometer. Ca^{2+} and Mg^{2+} were analysed by standard atomic absorption procedures and Na^+ and K^+ were determined by flame emission. Cl^- was determined using the method of Swain (1956). $\text{NO}_3\text{-N}$ (cadmium reduction), conductivity, pH, SO_4^{2-} and HCO_3^- were analysed by the methods of the American Public Health Association (APHA, 1975). Conductivity readings were corrected to 25°C (Golterman, 1970) and converted (micromho $\times 0.64$) to give an estimate of total dissolved solids (TDS).

July 1978 to May 1979. Figures in parentheses give the number of data points comprising the mean values for NO₃-N, Cl⁻ and TDS (10,) and pH, Na⁺, K⁺, Ca²⁺ and Mg²⁺ (,). The NO₃-N/Cl ratios are for mean NO₃-N and Cl concentrations.

Zone (1) Influenced by Ashburton and Rakai Rivers

	pH	NO ₃ -N/Cl	NO ₃ -N	Cl ⁻	SO ₄ ²⁻	*HCO ₃ ⁻	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	TDS
AR1 (10,5)	6.9±0.1	0.38	1.5±0.8	4.0±2.7	6.6±3.1	32.3±0.6	4.2±1.0	0.8±0.05	13.5±1.7	1.5±0.1	61.4±9.0
AR9 (9,4)	6.9±0.1	0.37	0.7±0.4	1.9±0.7	3.8±0.5	34.0±0.0*	2.3±0.2	7.0±0.0	11.2±0.6	1.0±0.0	49.5±2.1
AR13 (10,5)	6.7±0.2	0.58	1.4±0.3	2.4±0.5	4.9±0.5	35.7±1.2	3.5±0.2	0.9±0.05	11.4±0.4	1.8±0.1	59.1±3.0
AR18 (10,5)	6.6±0.1	1.18	2.0±0.6	1.7±0.4	4.8±1.0	33.3±5.0	3.1±0.3	0.7±0.1	11.2±0.7	2.1±0.1	59.4±3.4
AR25 (6,2)	-	0.22	0.8±0.4	3.7±1.9	3.0±0.0	-	2.9±0.1	0.7±0.0	10.6±0.6	1.5±0.0	66.0±10.1
AR26 (5,1)	-	0.30	1.0±0.5	3.3±0.6	5.0	-	6.6	-	14.0	-	58.8±6.0

Zone (2) Beneath non-irrigated pasture

AR2 (10,5)	6.9±0.1	0.34	7.3±0.5	21.0±1.4	6.2±1.8	44.3±0.6	15.8±0.8	1.5±0.05	16.7±1.0	5.3±0.3	140.0±2.6
AR3 (8,5)	7.5±0.2	0.37	4.9±0.3	13.3±1.3	1.2±0.4	54.7±0.6	8.1±0.4	1.4±0.05	19.6±0.1	3.4±0.1	113.0±2.2
AR4 (9,4)	6.7±0.1	0.33	9.0±1.0	17.1±2.5	10.5±1.9	41.5±2.1	18.2±2.1	1.4±0.05	17.6±0.3	5.5±0.2	143.0±9.9
AR5 (10,5)	6.5±0.4	0.49	11.2±2.5	22.8±3.4	14.6±1.9	46.3±2.3	20.9±1.6	1.4±0.05	19.6±0.8	9.8±0.6	182.5±7.7
AR6 (9,5)**	6.5±0.3	0.46	18.0±5.2	18.7±1.8	7.4±4.3	20.5±5.0	20.3±1.8	1.7±0.1	20.4±2.7	5.8±0.7	172.0±23.0
AR7 (10,5)	6.2±0.2	0.45	9.0±1.9	20.1±1.4	6.2±1.3	35.3±5.5	14.9±2.0	1.5±0.05	16.1±1.3	6.0±0.7	137.9±12.8
AR8 (9,4)	6.8±0.3	0.38	5.1±0.3	13.6±1.1	8.3±1.0	45.0±0.0*	12.3±0.6	1.3±0.05	16.2±0.6	3.5±0.1	144.4±1.5
AR10 (10,5)	6.0±0.1	0.36	4.9±1.0	13.8±1.5	4.0±0.0	62.0±0.0*	11.6±0.6	1.4±0.05	15.9±1.1	4.5±0.3	122.9±0.0
AR12 (10,5)	7.5±0.2	0.55	3.3±0.7	6.0±0.8	1.0±0.0	71.0±6.0	1.1±0.5	1.1±0.05	17.1±0.5	4.5±0.1	103.1±1.5
AR16 (9,5)	7.5±0.0	0.35	2.4±0.3	6.7±0.9	3.6±0.5	56.5±0.7	7.7±0.3	1.1±0.05	14.1±0.6	2.8±0.05	89.0±3.0

Zone (3) - Beneath non-irrigated pasture adjacent to Southern Alps.

AR21 (9,5)	6.2±0.2	1.19	3.1±1.0	2.6±0.8	7.2±0.8	19.0±2.6	3.9±0.2	0.7±0.05	10.3±0.7	1.6±0.2	60.7±7.0
AR22 (10,5)	6.0±0.1	0.88	2.3±0.8	2.6±0.7	3.8±0.4	39.3±0.6	3.8±0.1	0.6±0.0	14.3±1.1	1.7±0.2	63.9±11.4
AR23 (10,5)	6.2±0.1	0.91	2.0±0.7	2.2±0.6	1.8±0.4	20.0±2.0	3.1±0.2	0.5±0.05	8.1±0.3	1.4±0.1	45.6±2.8
AR24 (5,4)**	6.1±0.1	0.93	7.8±1.7	8.4±1.1	6.3±1.2	62.7±0.6	8.0±0.8	1.4±0.1	28.9±3.9	4.3±0.5	138.1±12.2

Zone (4) - Beneath border-dyke irrigated pasture

AR1 (10,5)	7.5±0.2	0.91	6.4±0.3	7.0±1.0	5.6±0.5	57.7±11.2	11.4±0.3	1.3±0.05	15.1±1.0	5.7±0.5	118.1±3.0
AR4 (8,5)**	6.7±0.2	0.76	3.7±0.3	4.9±0.6	7.6±0.5	35.3±1.5	5.9±0.4	1.0±0.1	13.2±0.3	2.6±0.1	81.0±1.8
AR5 (8,4)	6.6±0.1	0.83	6.6±0.6	8.0±0.6	5.8±0.5	67.0±1.0	10.6±0.3	1.3±0.05	17.8±0.2	6.8±0.2	127.5±2.4
AR7 (9,5)	7.0±0.5	1.33	10.4±0.4	7.8±0.3	8.4±1.1	40.0±1.0	11.0±0.2	1.1±0.05	18.5±0.3	5.0±0.2	128.9±1.3
AR9 (9,5)	6.8±0.1	1.47	5.6±0.7	3.8±0.6	5.6±0.5	35.3±1.5	6.8±0.3	0.8±0.05	13.9±1.0	2.6±0.05	85.7±2.8
AR20 (9,5)	6.4±0.1	1.67	9.2±1.4	5.5±0.9	9.2±2.3	27.0±1.7	8.5±0.3	1.2±0.05	18.7±3.0	3.6±0.2	106.0±8.4

† 2 or 3 data points.

* 2 data points.

** anomolous composition, classified by location (see text)

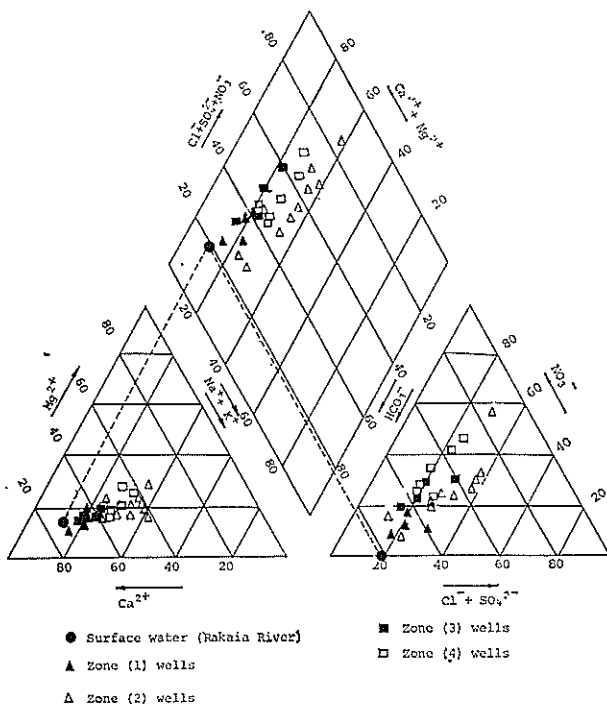


FIG. 2—Chemical analyses of Ashburton-Rakaia groundwater and Rakaia River represented as percentages of total equivalents per litre.

AREAL PATTERNS

Ashburton-Rakaia groundwater may be classified into four chemical zones (Table 2 and Fig. 2), three of which coincide with zones classified on the basis of nitrate-N and chloride concentrations by Quin and Burden (1979). The location and geographical extent of the zones (Fig. 1) are principally governed by the relative volumes and composition of different sources of groundwater.

Zone (1)

Zone (1) groundwater (Fig. 1) lies adjacent to regions of recharge from the Ashburton and Rakaia Rivers. Groundwater in the zone is characterised by high proportions of Ca^{2+} and HCO_3^- and low proportions of Na^+ , Cl^- , NO_3N and closely reflects the chemical composition of surface waters in the region (Fig. 2). The concentrations of NO_3N ($< 4 \text{ g/m}^3$) and Cl^- ($< 4 \text{ g/m}^3$) are consistently low (Table 2).

Gaugings on the Rakaia River indicate low-flow losses to groundwater of 15 to 20 m^3/s between Barrhill and the coast (Scott *et al.*, in prep.). The extent of zone (1) groundwater adjacent to the lower reaches of the

Rakaia confirms that the river is an important source of groundwater. Upstream of Barrhill flow gaugings suggest the river is perched, but the absence of wells in the north-western part of the study area prevents confirmation. Although well AR25 is classified in zone (1) its chemical composition is not necessarily characteristic of groundwater in the north-western region. The well is located on the lowest terrace of the Rakaia River about 50 m from an active channel and appears to be fed directly from the river. A similar argument may be applied to well AR13 which is located very close to the Ashburton River and does not necessarily indicate the presence of zone (1) groundwater. Flow gaugings indicate no loss of Ashburton River water over the reach (Scott *et al.*, in prep.).

The north Ashburton River (Fig. 1) recharges groundwater at a low flow rate of 3 to 4 m³/s (Scott *et al.*, in prep.). The presence of zone (1) groundwater adjacent to the Ashburton River confirms the flow losses and demonstrates that this reach of the Ashburton River is in hydraulic contact with groundwater. The extent of zone (1) is poorly defined in this area, but the flow loss gaugings suggest an appreciable region of groundwater is affected by the Ashburton River.

Some of the water in zone (1) is not in a pristine state, as illustrated by elevated (>1 g/m³) NO₃-N concentrations (Table 2). Nitrate leached from grazed pasture is the principal source of groundwater contamination (Quin and Burden, 1979).

Zone (2)

Zone (2) groundwater (Fig. 1) is located beneath mainly non-irrigated pasture that is not near regions of river recharge. Groundwater in zone (2) appears to be recharged by drainage from non-irrigated pasture and by down-gradient flow from other chemical zones, with drainage being the major source of shallow groundwater.

The composition of drainage from non-irrigated pasture is a combination of chemical species in precipitation and those leached from the soil. In coastal regions, precipitation chemistry quite closely reflects the relative abundance of the major anions and cations in seawater (Junge and Werby, 1958). Consequently, the relative abundance of the major ions in precipitation are Na⁺>Mg²⁺>Ca²⁺ and Cl⁻>SO₄²⁻>HCO₃⁻>NO₃-N.

The composition of precipitation is modified during drainage through the soil by the leaching of NO₃-N from the root zone of grazed pastureland (Quin, 1979) and by the displacement of SO₄²⁻ derived from regular applications of superphosphate to mid-Canterbury pastures. Some displacement of Ca²⁺ and Mg²⁺ from the soil exchange complex by Na⁺ may further modify the composition of the drainage water. Finally, dissolution of silicate minerals in the aquifer matrix may contribute further Na⁺, K⁺, Ca²⁺, Mg²⁺ and HCO₃⁻. Subsurface weathering of the mineral components of greywacke based material is, however, quite slow and the contribution of ions to groundwater from that source is probably comparatively small (Downes, 1980).

The concentrations of major ions in zone (2) groundwater are spatially variable (Table 2), presumably because in some areas the overlying land is spray irrigated and in other areas groundwater lies immediately down-gradient of another chemical zone (Fig. 1). Mean NO₃-N concentrations

for zone (2) wells range from 2.4 to 11.2 (excluding AR6) but the $\text{NO}_3\text{-N}/\text{Cl}^-$ ratios lie within a much narrower range (0.33 to 0.55). If the $\text{NO}_3\text{-N}$ and Cl^- in groundwater are derived mainly from rainfall drainage then the narrow $\text{NO}_3\text{-N}/\text{Cl}^-$ range indicates a uniform drainage composition. The wide range of $\text{NO}_3\text{-N}$ and Cl^- concentrations probably results from mixing of larger or smaller volumes of drainage with groundwater. The proportion of drainage in groundwater is influenced by proximity to regions of river recharge and depth below water table. A general increase in dissolved solids concentrations away from regions of river recharge (Table 2) indicates an increasing proportion of drainage in groundwater. Changes in groundwater composition with depth are discussed in more detail later.

The high $\text{NO}_3\text{-N}$ concentrations in zone (2) groundwater relative to zone (1) result mainly from nutrient leaching of grazed pasture (Quin and Burden, 1979). In mid-Canterbury, $\text{NO}_3\text{-N}$ leaching from non-irrigated pasture has been estimated to amount to 10 to 20 kg/ha annually and to produce concentrations of between 4 and 10 g/m³ in drainage (Quin, 1979). $\text{NO}_3\text{-N}$ concentrations in groundwater of about 10 g/m³ probably indicate, therefore, that drainage constitutes approximately 100 percent of the shallow groundwater. Wells AR4, AR5 and AR7 all penetrate less than 10 m below the water table and have $\text{NO}_3\text{-N}$ concentrations (Table 2) that suggest the shallow groundwater is comprised almost entirely of drainage.

The $\text{NO}_3\text{-N}$ concentration of well AR6 (mean 18.0 g/m³) is almost double that of nearby wells in zone (2) and $\text{NO}_3\text{-N}$ dominates its anion field (Fig. 2). Its cation composition however is similar to that of other zone (2) wells. Although cropland near well AR6 is spray irrigated, and irrigation increases nitrate leaching (Turner *et al.*, 1979) it seems unlikely that such high nitrate-N concentrations (up to 25.1 g/m³) would persist up to 17 m below the water table in a single localised area. Well AR6 exhibits anomalously large seasonal concentration fluctuations (Fig. 4) that suggest the well may be drawing-in water from very close to the water table. Corrosion of the well casing at the water table is, however, unlikely because the casing was replaced only six months prior to the sampling program. The septic tank disposal pit on the property is located approximately 60 m down-gradient of well AR6 and may be discounted as a source of $\text{NO}_3\text{-N}$ in the well water. At present, there appears to be no satisfactory explanation for the composition of groundwater from well AR6.

Zone (3)

Groundwater in zone (3) is located beneath non-irrigated pasture that is adjacent to the foothills of the Southern Alps. Drainage from the pastureland and runoff from the foothills recharge groundwater. There appears to be no hydraulic contact between Ashburton and Rakaia Rivers and zone (3) groundwater (Scott *et al.*, in prep.).

The relative proportions of most major ions in zone (3) groundwater are very similar to those in zone (2). This is probably because the composition of groundwater in both zones is strongly influenced by drainage from non-irrigated pasture. However, the proportions of Na^+ and Cl^-

are lower in zone (3) (Fig. 2) and the absolute ionic concentrations in zone (3) are generally two to three times less than in zone (2) (Table 2). The relatively low proportion of Cl^- is reflected in the high $\text{NO}_3\text{-N}/\text{Cl}^-$ ratios relative to zone (2) groundwater. A $\text{NO}_3\text{-N}/\text{Cl}^-$ ratio of 0.70 was selected as the boundary between zone (2) and zone (3) groundwater. There are two factors which cause the groundwater composition in zone (3) to differ from that in zone (2). First, the concentrations of Na^+ and Cl^- in precipitation (derived principally from sea-spray) decrease rapidly away from a coastline (Junge and Werby, 1958). In the Ashburton-Rakaia region the Cl^- content of precipitation decreases from 15 g/m^3 to 5 g/m^3 over a distance of 15 km from the coast. Secondly, annual precipitation increases from about 600 mm at the coast to above 1100 mm at the foothills but evapotranspiration remains fairly uniform throughout the Ashburton-Rakaia region (Scott *et al.*, in prep.). Drainage entering zone (3) groundwater might be expected, therefore, to have a larger volume (perhaps as much as 500 mm/a more than at the coast), but have a significantly lower concentration of Na^+ and Cl^- than drainage near the coast. This second factor almost certainly accounts for the relatively low absolute ionic concentrations in zone (3) groundwater. Clearly, the boundary between zones (2) and (3) is not sharp because the composition of groundwater beneath non-irrigated pasture changes progressively with distance from the coast.

The concentrations of major ions in well AR24, except for SO_4^{2-} , are significantly greater than in other wells in zone (3) (Table 2). The relatively high $\text{NO}_3\text{-N}/\text{Cl}^-$ ratio in well AR24 distinguishes it from groundwater in zone (2). The comparatively high $\text{NO}_3\text{-N}$ concentration ($7.8 \pm 1.7 \text{ g/m}^3$) in well AR24 may result from greater nitrogen mineralisation in the deeper soils in that area (Quin and Burden, 1979), but this process does not explain the other high ionic concentrations. Seepage from a sewage effluent irrigation scheme servicing the settlement around High-bank Hydro Power Station may cause the anomalous composition of well AR24. The relatively low level of SO_4^{2-} may be explained by incorporation of SO_4^{2-} from the irrigated effluent into soil organic matter (Quin, 1978).

Zone (4)

Zone (4) groundwater lies beneath and immediately downstream of the Ashburton-Lyndhurst Irrigation Scheme, except where the Ashburton River recharges groundwater (Fig. 1). Drainage from the irrigation scheme has a dominating effect on the composition of shallow groundwater (<30 m below water table) and accounts for the significantly higher ionic concentrations in zone (4) groundwater relative to zone (3) (Table 2).

The composition of zone (4) groundwater is similar to that of zone (2) except for a comparatively high $\text{NO}_3\text{-N}/\text{Cl}^-$ ratio (Table 2) and relatively low proportions of Na^+ and Cl^- (Fig. 2). The low proportions of Na^+ and Cl^- may result from the influx of drainage, containing less Na^+ and Cl^- than precipitation drainage, from the Ashburton-Lyndhurst Irrigation Scheme. Water for the irrigation scheme comes from the Rangitata River via a diversion race and therefore probably has a similar composition ($\text{Ca}^{2+} \gg \text{Na}^+$ and $\text{HCO}_3^- \gg \text{Cl}^-$) to the Ashburton and Rakaia

Rivers (Fig. 2). Dissolved species in irrigation water are concentrated less by evapotranspiration than those in precipitation because about two-thirds of the irrigation water (Fitzgerald, 1974) but only about one-third of the precipitation (Scott, *et al.*, in prep.) drains to groundwater.

Two factors appear to contribute to the high $\text{NO}_3\text{-N}/\text{Cl}^-$ ratios of zone (4) groundwater. First, the comparatively low Cl^- concentration in irrigation drainage tends to increase the $\text{NO}_3\text{-N}/\text{Cl}^-$ ratio of adjacent groundwater relative to zone (2). Second, $\text{NO}_3\text{-N}$ leaching from irrigated pasture is significantly greater than from non-irrigated pasture. Quin (1979) estimated $\text{NO}_3\text{-N}$ leaching to amount to approximately 100 kg/ha from irrigated pasture, and to produce concentration of 14 to 17 g/m³ in drainage. The $\text{NO}_3\text{-N}$ concentrations in zone (4) groundwater do not exceed those in zone (2) by as much as might be expected from the masses of $\text{NO}_3\text{-N}$ leached from irrigated and non-irrigated pastures because of dilution by the large volume of irrigation water that drains to groundwater.

CHANGES WITH DEPTH

Although the proportions of major ions in groundwater are similar within both zone (2) and zone (4), the absolute ionic concentrations within each zone cover a wide range (Table 2). Differences in the magnitudes of concentrations within zones (2) and (4) appear to be principally related to the depth of well screens below the water table. The gross chemistry of both groundwater zones is strongly influenced by subsurface drainage of irrigation water and/or precipitation. Groundwater near the water table has a composition very similar to that of subsurface drainage, but contains progressively less drainage (lower Na^+ , Cl^- and $\text{NO}_3\text{-N}$) and more river-derived water (higher Ca^{2+} and HCO_3^-) with increasing depth (Fig. 3). The drainage component of groundwater persists to a greater depth near the coastline because drainage constitutes a progressively greater proportion of the total groundwater flow with increasing distance from the regions of river recharge. $\text{NO}_3\text{-N}$ contamination of groundwater persists to a greater depth below the Ashburton-Lyndhurst Irrigation Scheme because the volume of drainage from irrigated pasture is significantly greater (~ three fold) than that from non-irrigated pasture (Quin and Burden, 1979).

The more uniform composition of zone (1) groundwater (Table 2) may be attributed to two factors. First, although the depth below water table of most zone (1) wells is unknown, wells near the Ashburton and Rakaia Rivers are almost exclusively shallow (Scott, 1980). Any changes in groundwater composition with depth are, therefore, unlikely to be apparent in the observation wells. Secondly, groundwater in zone (1) largely reflects the composition of local rivers which have uniformly low concentrations of ionic constituents. A similar explanation probably applies to the relatively uniform composition of zone (3) wells. All typical zone (3) wells reflect the composition of drainage from non-irrigated pasture which is the principal source of recharge in that area. Furthermore, because the foothills constitute the inland boundary of the Ashburton-Rakaia aquifer system, the composition of zone (3) groundwater is not affected by down-gradient flow from another region.

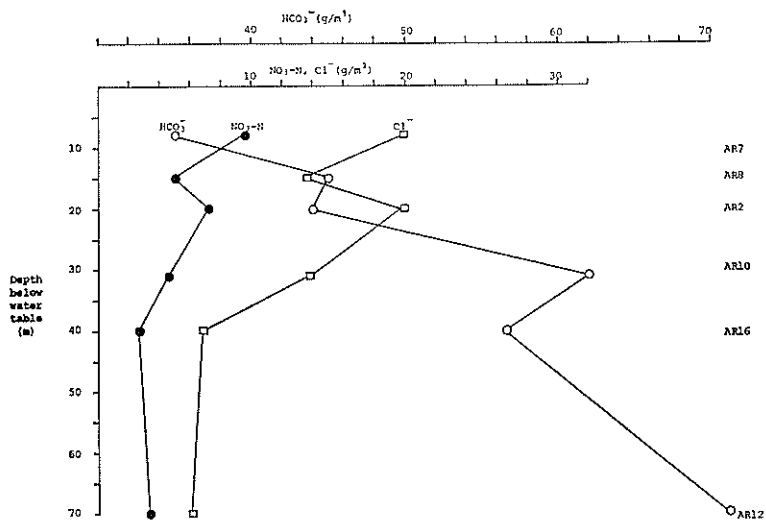


FIG. 3—Changes in groundwater composition for zone (2) wells with increasing depth below the water table. Concentrations are means of up to 10 values.

TEMPORAL FLUCTUATIONS

Seasonal changes in the chemical composition of a water-table aquifer are principally governed by the influx of drainage from the land surface. When rainfall or irrigation exceeds soil moisture capacity, solutes are both leached to groundwater and incorporated by a rising water table (Burden, 1980). Temporal fluctuations in the chemical composition of groundwater from Ashburton-Rakaia wells may be classified into four groups: (1) shallow wells (< about 20 m) in areas of non-irrigated pastureland, (2) deep wells (> about 20 m) in areas of non-irrigated pastureland, (3) wells in regions of river recharge, and (4) wells in areas of irrigated pastureland.

Shallow wells (AR 4, 5, 6, 7 and 8) in areas of non-irrigated pastureland generally exhibit a seasonal trend in major ion chemistry that correlates well with the seasonal pattern of precipitation drainage. NO₃-N, Cl⁻ and TDS (conductivity) concentrations alone were measured throughout the present sampling program. The concentrations of the other major ions were recorded on, at most, the first five sample rounds so the observed temporal fluctuations in their concentrations were not entirely satisfactory for statistical analysis. However, variations in Cl⁻, SO₄²⁻, Na⁺, K⁺, Ca²⁺ and Mg²⁺ concentrations in shallow wells appear to correlate significantly with NO₃-N concentrations (Table 3); therefore, temporal variations in NO₃-N levels have been plotted to describe the fluctuations in all seven constituents (Fig. 4). Fluctuation in the concentration of HCO₃⁻ tends to be negatively correlated with the other major ions suggesting that the HCO₃⁻ ions come from a different source. Subsurface drainage

TABLE 3—Correlation matrix of major-ion concentrations in groundwater from shallow Ashburton-Rakaia wells (AR1, 4, 5, 6, 8, 17, 19-24 and 26). Figures in parentheses give the number of data points.

	SO ₄ ²⁻	Cl ⁻	NO ₃ -N	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺
HCO ₃ ⁻	0.26(34)	0.36(33)	0.37(34)	0.42(34)	0.59(34)†	0.49(34)*	0.79(34)†
SO ₄ ²⁻	—	0.65(56)†	0.66(57)†	0.75(57)†	0.64(57)†	0.67(54)†	0.52(56)†
Cl ⁻	—	—	0.70(108)†	0.94(57)†	0.80(57)†	0.69(56)*	0.44(56)*
NO ₃ -N	—	—	—	0.77(58)†	0.78(58)†	0.62(57)†	0.67(57)†
Na ⁺	—	—	—	—	0.83(58)†	0.91(55)†	0.52(57)†
K ⁺	—	—	—	—	—	0.82(55)†	0.73(56)†
Mg ²⁺	—	—	—	—	—	—	0.59(54)†

† Values significant at the 0.1% level

* Values significant at the 1% level

is clearly the principal source of NO₃-N, Cl⁻, SO₄²⁻, Na⁺, K⁺, and Mg²⁺ in shallow groundwater. A close correlation between NO₃-N and TDS concentrations suggest that the increase in NO₃-N content of groundwater in winter is caused by a change in the volume of precipitation drainage entering groundwater and not seasonal changes in the NO₃-N concentration of that drainage. From consideration of the volume of winter drainage, larger seasonal concentration peaks might be expected in Ashburton-Rakaia wells (Burden, 1980). The preponderance of relatively small peaks for Ashburton-Rakaia wells indicates that seasonal changes in groundwater composition are rapidly damped with increasing depth below the water table. The anomalous NO₃-N concentrations in well AR6 have been discussed previously.

Deep wells (AR2, 3, 10, 12 and 16) in areas of non-irrigated pastureland show no recognisable trend in NO₃-N concentrations with time (Fig. 4). The deep wells are apparently unaffected by the seasonal pattern of drainage because dispersion rapidly homogenises the chemical composition of groundwater. Variations in the composition of groundwater more than about 20 m below the water table probably represent the magnitude of background fluctuations caused by incomplete mixing of waters from different sources.

In areas affected by river recharge, wells (AR1, 9, 13 and 18) exhibit a weak seasonal trend in NO₃-N concentration (Fig. 4). The weak trend may indicate either that drainage from the land affects the composition of groundwater, even when it is located close to an influent river reach, or that seasonal changes in the composition of river water are reflected in the adjacent groundwater. Seasonal variations in NO₃-N concentrations appear to be larger for higher absolute concentrations suggesting that drainage is the principal factor causing the small variations in groundwater composition. The record for wells AR 25 and 26 are too short to establish a seasonal correlation.

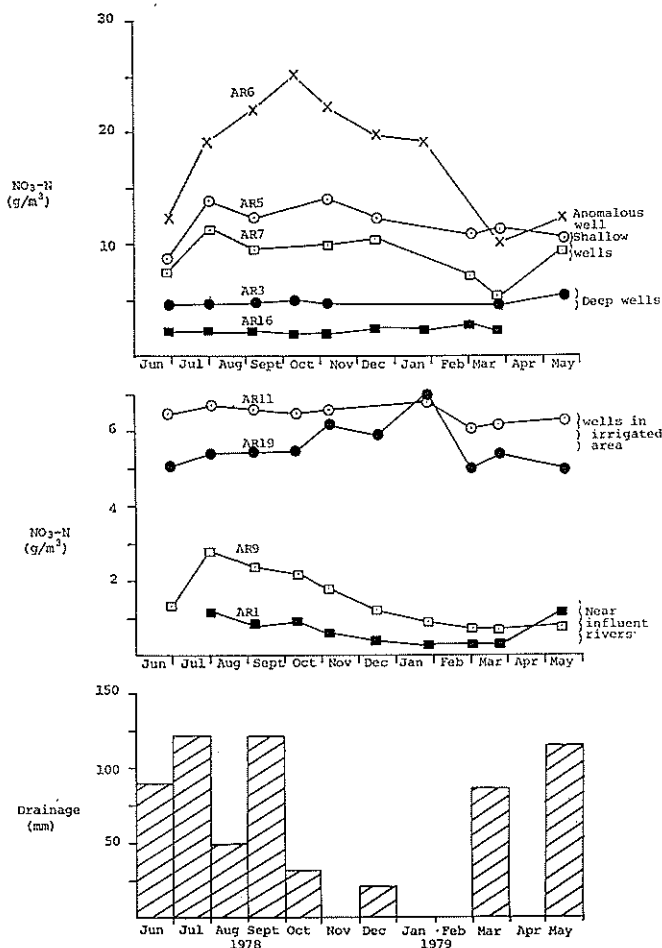


FIG. 4—Comparison of $\text{NO}_3\text{-N}$ concentrations in Ashburton-Rakaia wells with monthly estimates of subsurface drainage for the period June 1978 to May 1979. Drainage was computed from daily rainfall and mean (1950-1978) pan evaporation data.

The fourth group of wells (AR11, 15, 17, 19 and 20) lie within the area of the Ashburton-Lyndhurst border-dyke irrigation scheme. $\text{NO}_3\text{-N}$ concentrations in these wells are greatest during the irrigation season (late October to early March) (Fig. 4). The high $\text{NO}_3\text{-N}$ concentrations through the summer are not related to an increase in the $\text{NO}_3\text{-N}$ content of drainage because the drainage composition remains quite uniform throughout

the year (Quin and Burden, 1979). The volume of drainage, however, is not evenly distributed. Drainage amounts to 400–600 mm during an irrigation season (5–6 months), compared to 200–300 mm throughout the rest of the year (Fitzgerald, 1974). During summer, therefore, drainage comprises a larger portion of shallow groundwater beneath irrigated pastureland than during winter, and $\text{NO}_3\text{-N}$ concentrations in groundwater are accordingly higher.

ACKNOWLEDGEMENTS

The author is grateful to David Scott for the drainage computation and to Murray Close for chemical analyses. The Commissioner of Works has given permission for this publication.

REFERENCES

- American Public Health Association, 1975: *Standard methods for the examination of water and wastewater*, 14th ed. Washington D.C. 1193 p.
- Burden, R. J. 1980: Distribution of nitrate-N concentrations in groundwater beneath intensively grazed pastureland in the Ngatarawa Valley, Hawkes Bay. *Journal of Hydrology (NZ)* 19 (2): 94-105.
- Downes, C. J. 1980: Chemistry of the Hutt Valley underground waters. Chemistry Division Unnumbered Report, *Department of Scientific and Industrial Research*, Lower Hutt, New Zealand. 38 p.
- Fitzgerald, P. D. 1974: The effect of climate on water use on Canterbury irrigation schemes. *Technical Report No. 8*. Winchmore Irrigation Research Station, Ministry of Agriculture and Fisheries, Ashburton, New Zealand. 20 p.
- Golterman, H. L. 1970: *Methods for chemical analysis of fresh waters*. International Biological Programme (I.B.P.) Handbook No. 8 Blackwell, London. 84 p.
- Junge, C. E. and Werby, R. T. 1958: The concentration of chloride, sodium, potassium, calcium, and sulphate in rain water over the United States. *Journal of Meteorology* 15 (5): 417-425.
- Maidment, D. R.; Lewthwaite, W. J. and Hamblett, S. G. 1980: Rakaia water use and irrigation development. *Water and Soil Miscellaneous Publication No. 19*. Ministry of Works and Development, Wellington, 47 p.
- Quin, B. F. 1978: The effects of drainage from surface irrigation with treated sewage effluent on groundwater quality at Templeton. *Journal of Hydrology (NZ)* 17 (2): 91-102.
- Quin, B. F. 1979: The effects of surface irrigation on drainage and groundwater quality pp. 139-145. In *"The quality and movement of groundwater in alluvial aquifers of New Zealand"*. Proceedings of a Symposium, Lincoln College, November 1978.
- Quin, B. F. and Burden, R. J. 1979: The effects of land use and hydrology on groundwater quality in mid-Canterbury, New Zealand. *Progress in Water Technology* 11 (6): 433-448.
- Rajagopal, R. 1978: Impact of land use on groundwater quality in the Grand Traverse Bay region of Michigan. *Journal of Environmental Quality* 7: 93-98.
- Saffigna, R. G. and Keeney, D. R. 1977: Nitrate and chloride in groundwater under irrigated agriculture in central Wisconsin. *Ground Water* 15: 170-177. Worthington, USA.
- Scott, D. M.; Thorpe, H. R. and Burden, R. J. in prep: Groundwater re-

- sources between the Rakaia and Ashburton Rivers. Water and Soil Division, Ministry of Works and Development, Christchurch.
- Scott, G. L. 1980: Near-surface hydraulic stratigraphy of the Canterbury Plains between Ashburton and Rakaia Rivers, New Zealand. *Journal of Hydrology (NZ)* 19 (1): 68-74.
- Spalding, R. F. and Exner, M. E. 1980: Areal, vertical and temporal differences in groundwater chemistry: I. Inorganic constituents. *Journal of Environmental Quality* 9 (3): 466-479.
- Suggate, R. P. 1973: Geological map of New Zealand, Sheet 21 (2nd ed.). Department of Scientific and Industrial Research, Christchurch.
- Swain, J. S. 1956: Absorptiometric determination of low concentrations of chlorides. *Chemistry in Industry* 29: 418-420.
- Turner, M. A.; Tillman, R. W. and Syers, J. K. 1979: Losses of phosphorus and nitrogen forms in subsurface drainage water as influenced by phosphate fertilizer, grazing animals and irrigation treatments. *Progress in Water Technology* 11 (6): 331-338.
- Walsh, R. P. and Scarf, F. 1980: The water resources of the Ashburton and Hinds Rivers. *Publication No. 21*. South Canterbury Catchment Board, Timaru, New Zealand, 40 p.
- Wilson, D. D. 1973: The significance of geology in some current water resources problems, Canterbury Plains, New Zealand. *Journal of Hydrology (NZ)* 12(2): 103-118.