

Hydrogeochemistry of the upper Hunter River valley, New South Wales

BMR Bulletin



J. R. Kellett, B. G. Williams, & J. K. Ward



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FOREWORD

There are many parts of Australia where major groundwater resources are coming under increasing stress or where there are potential or actual environmental problems related to groundwater. The Hunter Valley is one such area.

The upper Hunter Valley is one of Australia's most important mining, industrial, and agricultural regions. The demand of these three activities on the groundwater resources of the area is adversely affecting groundwater resources. Unless these water resources are carefully managed in the future it may be difficult to provide adequate supplies of good quality water to the region. Coupled with this, there are emerging problems with increasing land and river salinity.

Future management options will require detailed information on the hydrogeology of the region, including data on fluxes, flow paths, and residence times of groundwater. With this in mind, the BMR and CSIRO undertook a major hydrochemical study of the upper Hunter Valley. This report documents the results of the study and clearly demonstrates that man's activities are having, and will continue to have, a profound effect on water quality in the region. However, it must also be recognised that saline groundwater is a natural phenomenon of the Central Lowlands region which will continue to contribute a significant quantity of salt into the total groundwater and associated surface water systems.

It is clear that future salinity control measures will require even more detailed information on the chemistry both of the Hunter River and the return water flows to it in order to safeguard this area of enormous economic importance and great natural beauty.

Peter J. Cook. Chief, Division of Continental Geology.

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CONTENTS

ABSTRACT	ix
INTRODUCTION	l
Physiography and climate	l
General geology	l
Acknowledgements	
HYDROGEOLOGY	
Previous and current work	
Regional hydrodynamics	
Alluvial aquifers	
Fractured rock aquiters	
Groundwater flow rates	/ ي
HYDROGEOCHEMISTRY	
Ayurogeochemical survey and compliation of data	Uase
Hudrochomical provinces	
Solute behaviour in the hydrochemical provinces	10
Mineralogy and geochemistry	18
Salt efflorescences	22
Minor elements	23
Base flow in the upper Hunter River valley area	24
CHEMICAL EQUILIBRIA	
Data preparation	
Disequilibrium indices	
Simple carbonate minerals	
Complex carbonate minerals	
Simple sodium minerals	
Sulphate minerals	
Silica minerals	
The role of carbon dioxide	
Aluminosilicates	
STATISTICAL ANALYSIS	
VARIATION BETWEEN HYDROCHEMICAL	PROVINCES
Canonical variates	
Censoring and transformation of data	
Results	
Interpretation of the canonical vectors (i)	
Distances between groups	
Further partitioning of data	
Results	
Interpretation of the canonical vectors (11)	
Distances between subgroups	
Comparison of the canonical variates analyses	OVINCES 55
VARIATION WITHIN HTDROCHEMICAL PR	OVINCES
Methodology	50 51
Results	5
Interpretation of the principal components	50
Principal components from within groups covari	ance matrices 5
Principal components from pooled covariance m	atrix 6
Principal components from within groups correl	ation matrices
Principal components from pooled correlation m	atrix
Consistency of principal components analyses	
Clustering by principal components	
Interpretation of non-reactive groundwater mixing	g by principal components
The principal components of hydrochemical trend	Is and equilibria
SYNTHESIS	
DISCUSSION	
REFERENCES	
APPENDIXES (On microfiche-in-back pocket)	
Appendix 1. Chemical analyses-	APPENDICES
Appendix 2. Trace-element analyses	MGUGD
	NEVER

v

TABLES

1.	Stratigraphic units in the upper Hunter River valley	5
2.	Mean yield and depth of wells in the upper Hunter River valley and major tributary floodplains	6
3.	Estimated regional groundwater velocities for unconfined flow in the major lithological units of the upper Hunter River valley	7
4.	Correlation matrix of six major ions in upper Hunter River valley groundwater	8
5.	Hydrochemical provinces, upper Hunter River valley	10
6.	Solute concentrations in upper Hunter River valley hydrochemical provinces	10
7.	Mineralogy of salt efflorescences, upper Hunter River valley	23
8.	Change in mean HCO ₃ :Cl ⁻ ratios in base flow of Goorangoola-Glennies Creek valley	34
9.	Congruent solubility products of minerals.	39
10.	Canonical roots and vectors for upper Hunter River valley hydrochemical provinces, $(k=8)$	53
11.	Subdivision of upper Hunter River valley hydrochemical provinces for canonical variates analysis	55
12.	Canonical roots and vectors for upper Hunter River valley hydrochemical subgroups, $(k=25)$	56
13.	Principal components extracted from covariance and correlation matrices of upper Hunter River valley hydrochemical provinces	58
14.	Comparison of chemical facies from significant $Y_3(S)$ loadings for upper Hunter River valley hydrochemical province	59
15.	Correlation of principal components from pooled covariance matrix of upper Hunter River valley hydrochemical provinces	61
16.	Comparison of chemical facies from significant $Y_3(R)$ loadings from upper Hunter River valley hydrochemical provinces	62
17.	Correlation of principal component scores from pooled correlation matrix of upper Hunter River valley hydrochemical provinces	62
18.	Angles between corresponding sets of principal components derived from S and R matrices of six \log_{10} -transformed variables, upper Hunter River valley groundwater	63
	FIGURES	
1.	Locality map and generalised surface geology.	2
2.	Geomorphic subdivisions, Hunter River valley catchment (after Story & others, 1963).	3

- 3. Generalised geology and major structures, Hunter Valley Dome Belt.
- 4. Frequency distribution of anion and cation concentrations in upper Hunter River valley 9 groundwater.

4

- 5. Composition diagrams of chloride concentration versus total ions by hydrochemical 11 province.
- 6. Composition diagrams of bicarbonate versus chloride concentration by hydrochemical 12 province.
- Composition diagrams of sulphate versus chloride concentration by hydrochemical province and composition diagrams of normalised sulphate versus chloride concentration by hydrochemical province.
- 8. Composition diagrams of silica versus chloride concentration by hydrochemical 15 province.
- 9. Composition diagrams of calcium versus chloride concentration by hydrochemical 16 province.
- 10. Composition diagrams of magnesium versus chloride concentration by hydrochemical 17 province.
- 11. Composition diagrams of sodium versus chloride concentration by hydrochemical 18 province.
- 12. Composition diagrams of potassium versus chloride concentration by hydrochemical 19 province.
- 13. Variation in sulphur, sulphate and chloride content of coal seams from the Wittingham 21 and Greta Coal Measures.
- 14. Means and ninety-five per cent confidence intervals for B, P and Al concentration by 24 hydrochemical province.
- Longitudinal variation in concentration of major ions: (a) Hunter River, August 1982; (b)
 Wollombi Brook, 5, 6/8/82; (c) Glennies Creek, 16/8/82; (d) Goulburn River, 3, 4/8/82.
- 16. Longitudinal variation in (a) Wybong Creek, August 1982; (b) Martindale Creek, 4/8/82; 28
 (c) Sandy Creek, August 1982.
- 17. Longitudinal variation in concentration of major ions: (a) Saddlers Creek, 13–18/8/82; 30 (b) Baywater Creek, 13–18/8/82.
- 18. Longitudinal variation in concentration of major ions: (a) Bowmans Creek, 13, 14/8/82; 31
 (b) Swamp Creek, 15/8/82; (c) Muscle Creek, 20/8/82; (d) Stringybark Creek, 20/6/83;
 (e) Longitudinal variations in concentration of major ions and decline in HCO₃/Cl⁻ ratio, Goorangoola Creek, 16/8/82.

- 19. Longitudinal variation in concentration of major ions: (a) Main Creek, 17/8/82; (b) 35 Loder Creek, 9, 10/8/82.
- Longitudinal variation in concentration of major ions: (a) Spring Creek, 11–12/8/82; (b) 37 Big Flat Creek, 29/6/83.
- 21. Distribution of Disequilibrium Indices for the simple carbonate minerals calcite, 39 magnesite and natron in upper Hunter River valley groundwater.
- 22. Distribution of calcite, magnesite and natron Disequilibrium Indices by hydrochemical 40 province.
- 23. Distribution of Disequilibrium Indices for the complex carbonate minerals dawsonite, 41 dolomite, huntite and hydromagnesite in upper Hunter River valley groundwater.
- 24. Distribution of dolomite, huntite and hydromagnesite Disequilibrium Indices by hydrochemical province. 42
- 25. Distribution of Disequilibrium Indices for the simple sodium minerals halite, mirabilite 43 and natron in upper Hunter River valley groundwater.
- 26. Distribution of Disequilibrium Indices for the sulphate minerals gypsum, mirabilite, 43 bloedite and glauberite in upper Hunter River valley groundwater.
- 27. Distribution of gypsum, glauberite and bloedite Disquilibrium Indices by hydrochemical 44 province.
- 28. Distribution of Disequilibrium Indices for chalcedony, amorphous silica and sepiolite. 45
- 29. Distribution of chalcedony and sepiolite Disequilibrium Indices by hydrochemical 45 province.
- 30. Relationship between soluble silica and the groundwater carbon dioxide partial pressure, 46 upper Hunter River valley.
- 31. Distribution of carbon dioxide partial pressures in upper Hunter River valley groundwater. 46
- 32. The effect on groundwater pH upon reaching equilibrium with atmospheric carbon 46 dioxide.
- 33. The effect on calcite Disequilibrium Indices for (a) WO and GM groundwater upon reaching equilibrium with atmospheric carbon dioxide; the effect on sepiolite Disequilibrium Indices for (c) WO and (d) GM groundwater upon reaching equilibrium with atmospheric carbon dioxide.
- 34. Stability fields of some minerals in the Ca–Al–Si–H₂O system at 25°C as a function of Ca²⁺, H⁺ and soluble SiO₂. Points are from upper Hunter River valley groundwater and boundaries are from thermodynamic data of Stumm & Morgan (1970).
- 35. The relationship between the calcite Disequilibrium Index and the tendency for Camontmorillonite to form a stable phase in upper Hunter River valley groundwater.
- 36. Stability fields of some minerals in the Na–Al–Si–H₂O system at 25°C as a function of Na⁺, H⁺ and soluble SiO₂. Points are from upper Hunter River valley groundwater and boundaries (a) from thermodynamic data of Rai & Lindsay (1975) and (b) Stumm & Morgan (1970).
- 37. Stability fields of some minerals in the K-Al-Si-H₂O system at 25°C as a function of K⁺, H⁺ and soluble SiO₂. Points are from upper Hunter River valley groundwater and boundaries (a) from thermodynamic data of Garrels & Christ (1965) and (b) from Rai & Lindsay (1975).
- Canonical variate plot showing salinity and facies variations of upper Hunter River 53 valley groundwater. Based on six log₁₀-transformed variables. 95% confidence circles shown.
- 39. Canonical variate plot showing facies and silicate dissolution variations of upper Hunter River valley groundwater. Based on six log₁₀- transformed variables. 95% confidence circles shown.
- 40. Complete linkage dendrogram of upper Hunter River valley hydrochemical provinces 56 based on six log₁₀-transformed variables.
- Canonical variate plot showing salinity and facies variations of 25 subgroups of upper Hunter River valley groundwater. Based on six log₁₀-transformed variables. 95% confidence circles shown.
- 42. Complete linkage dendrogram of 25 subgroups of upper Hunter Valley groundwater 57 based on six log₁₀-transformed variables.

59

- 43. Sources of major ions in groundwater of the upper Hunter River valley.
- 44. Clustering by principal component scores of salinity and facies variations for 670 individuals of upper Hunter River valley groundwater. Based on six log₁₀-transformed variables. Principal components from pooled correlation matrix. (a) CARB-TRIAS, (b) WO, (c) HFP1, (d) HFP2, (e) W11, f) W12, (g) GM, (h) Hydrochemical processes represented by principal component scores. Mean scores of hydrochemical provinces shown.
- 45. Discrimination of zones of hydrodynamic mixing of upper Hunter River valley groundwater by principal component scores. Based on six log₁₀- transformed variables of 670 individuals. Principal components from pooled correlation matrix. Mean scores of hydrochemical provinces shown. (a) HFP1, (b) HFP2, (c) WO, (d) WI1.

46. Hydrochemical trends by principal component scores of baseflow water in some upper Hunter River valley streams. (a) & (b) Domains whose water has reached or exceeded equilibrium with respect to certain minerals shown. (c) Clustering by second and third principal component scores of facies variations for 670 samples of upper Hunter River valley groundwater. Clusters enclose at least 80% of scores for the hydrochemical subgroup shown.

68.

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PLATES

1. Geology of the upper Hunter River valley, 1:100 000-scale map.

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2. Hydrochemical provinces and sampling locations of the upper Hunter River valley, 1:100 000scale map.

ABSTRACT

The chemistry of groundwater in the regional recharge zones of Triassic and Carboniferous rocks in the upper Hunter River valley of New South Wales is strongly influenced by silicate and carbonate dissolution/ precipitation reactions, ion exchange and the dispersion of aerosols in infiltrated rainfall. The Wollombi Coal Measures and Jerrys Plains Subgroup of the Wittingham Coal Measures west of the Muswellbrook Anticline constitute the regional groundwater transmission zones, and the processes having the greatest influence on the chemistry of their water are dissolution/precipitation reactions and oxidation of coals. The semi-confined aquifers of the Greta Coal Measures, Maitland Group, Dalwood Group, and Wittingham Coal Measures in the eastern and southern parts of the valley discharge into unconfined sand and gravel aquifers of the Hunter River floodplain. These Permian rocks are the source of the most saline water in the valley, and the chemistry of their groundwater is largely determined by oxidation of sulphides and molecular diffusion of connate marine salts, a legacy of periodic immersion by Permian ocean water.

Disequilibrium indices for calcite, dolomite and dawsonite indicate that these carbonates are being precipitated today in the groundwater of the Central Lowlands provinces; they are being dissolved in the southern and western groundwater recharge zones and are in equilibrium with water of the northern recharge zone. The iron carbonates, siderite and ankerite, are a product of a palaeohydrochemical regime characterised by saline alkaline water rich in dissolved iron disseminated from gels originally accumulated in the Permian peat swamps, but these minerals are not being precipitated in modern upper Hunter River valley groundwater. The sulphate minerals, gypsum, thenardite and bloedite, occur extensively in salt efflorescences in the Permian rocks of the Central Lowlands, but their disequilibrium indices show that none of the minerals can be precipitated in the contemporary upper Hunter River valley groundwater by processes other than evaporative concentration. Models based on incongruent dissolution of feldspars allocate much of the upper Hunter River valley groundwater to the kaolinite stability field, which is consistent with the abundance of kaolinite as an authigenic mineral in the fractured rocks are accumulating in the groundwater sinks around the margins of the Hunter River floodplain, as indicated by the large proportion of groundwater in these areas which are in equilibrium with Ca-montmorillonite.

Concentrations of Ca^{2+} , SiO_2 and HCO_3^- ions in upper Hunter River valley groundwater approach log-normal distributions and these species are most highly identified with continental hydrochemical processes. In contrast, the four 'elements' constituting the bulk of solutes in ocean water, Cl^- , Na^+ , SO_4^{2-} and Mg^{2+} , are distributed in two modes: the low-concentration primary mode, representing the dissemination of these species from the continental solutes store, and the secondary high-concentration mode, reflecting diffusion and oxidation of marine inputs.

On a province-wide scale, composition diagrams of solute behaviour identify the Wittingham Coal Measures to the east and south of Muswellbrook Anticline, the Greta Coal Measures, and the Maitland and Dalwood Groups as systems that can be approximated by simple linear mixing models between meteoric and oceanic water. Composition diagrams for the floodplain hydrochemical provinces show that the alluvial aquifers can be represented as mixing systems between Hunter River surface water and groundwater of the fractured-rock aquifers.

Principal component analyses describe the chemical evolution of upper Hunter groundwater from the Permian marine transgression through to the present continental leaching regime — for similar positions along flow lines in discharge zones, groundwater of the Greta Coal Measures, Maitland Group and Wittingham Coal Measures east of the Muswellbrook Anticline have not advanced past the first stage of the evolutionary sequence Na⁺– Cl^{-} \rightarrow Na⁺– HCO_{3}^{-} —> Ca²⁺– HCO_{3}^{-} ; groundwater of the Wittingham Coal Measures west of the Muswellbrook Anticline has attained the second stage of this evolution as a consquence of a longer history of flushing by meteoric water and prior thermal mobilisation of interstitial fluid in areas peripheral to Tertiary dolerite intrusives.

Discrimination of hybrids according to their first and second principal component scores shows that in the floodplain alluvium significant quantities of groundwater with the chemical signature of Maitland Group rocks emanate from the Aberdeen and Hunter Thrust Faults, the Hilliers Creek Valley and the Neotsfield area. Input of groundwater from the Wittingham Coal Measures occurs at Jerrys Plains and Alcheringa; the latter mixing zone is of special significance because the source is sufficiently strong to overprint the role of the Hunter River as a dividing streamline for groundwater flow. The strongest sources of Wittingham groundwater are those upwelling along the northern end of the Mount Ogilvie Fault. Their dispersion into the groundwater of the Triassic rocks and Woollombi Coal Measures is reflected by a saline pulse in principal component scores of nearby bores and wells.

Canonical variates analyses confirm that geology is the dominant control in the chemistry of upper Hunter River valley groundwater. It should be recognised that high background salinity in groundwater of the Central Lowlands is a natural phenomenon that will persist for the foreseeable future.

INTRODUCTION

The upper Hunter River valley area of New South Wales (Fig.1) has the largest exploitable deposits of Permian bituminous coal in the Sydney Basin. Raw coal production in 1983 was 23.3 million tonnes, mostly by open-cut mining. In recent years the upper Hunter has assumed increasing importance as a centre of power generation and industrial development. The valley is also a prime area of agricultural production, and as rural land has gradually been modified by industrial development, demand on water resources and concern about future water quality have increased.

By the year 2000, it is estimated that 46 per cent of water demands above Maitland will be for industrial consumption compared with 26 per cent for irrigated agriculture (Garman, 1982). Much of the industrial activity centres around coal mining, and involves the interception, use, and disposal of groundwater. Similarly, power-generation industries require cooling water, resulting in evaporative concentration of soluble salts, which need to be disposed of. No attempt has been made on a regional scale to determine the salt returned to surface water from agricultural activities, but soluble salt concentrations in surface run-off from 'natural' pasture and mine-spoil materials range from 140 mg/L to 1260 mg/L (Gates & Kalf, 1983). Gates & Kalf also noted that groundwater in spoil piles is likely to have considerably higher salt concentrations than that in the surrounding undisturbed rocks.

Detailed monitoring of surface water indicates that base-flow contributions have a marked effect on quality. Under dryweather conditions, the electrical conductivity of the Hunter River increases from about 400 μ S.cm-1 just below the Glenbawn Dam (Fig. 1) to 1000 μ S.cm-1 at Maitland, about 250 km downstream. At least part of this increase is due to geological influences on groundwater quality (Garman, 1982). Water quality in the Hunter River is controlled by releases of stored surface water and by the disposal of industrial waste water under high-flow conditions. Disposal of waste water is subject to legislative controls.

It is clear that future control measures will require detailed information on the chemistry of both the Hunter River and the return flows to it. This report indicates various approaches to the interpretation of groundwater chemistry that may be useful in analysing the system, particularly in defining the chemical signature of various water sources. Restricted access to a number of mine sites for groundwater samples has, however, limited detailed interpretation in some areas.

Physiography and climate

The groundwater survey covers the central Hunter–Goulburn River valley system, and therefore includes the major geomorphic regime of the catchment (Fig. 2), the Central Lowlands (Story & others, 1963). The Central Lowlands are traversed by the Hunter River and its major tributaries, and are surrounded by steep slopes, rugged ranges, and, in places, elevated plateaus.

The physiography is strongly controlled by the underlying geology (Fig.2 & Pl. 1). The Southern Mountains region consists of rugged Triassic sandstone mountains up to 1000 m and deeply incised valleys; soils are generally shallow because the Triassic sandstones are resistant to chemical weathering. At the junction of the Southern Mountains with the Central Lowlands, discontinuous sheets of quartzose sand fan out from the foothills for 1-2 km.

To the west, the Central Goulburn valley region is similar to the Southern Mountains; it is underlain by Triassic sandstones and shales, and consists of irregular steep-sided hills and plateaus, and deeply incised rivers. The Merriwa Plateau region in the northwest consists of rolling to hilly terrain, developed as a planation surface on extensive Tertiary basalt flows. Lavas have partially filled pre-existing valleys, and post-volcanic streams have incised on either side of the flows, forming sub-parallel valleys that reflect the pre-basalt drainage. The degree of incision has been controlled by uplift, and by marked variations in relative sea level during the Cainozoic.

Resistant folded Devonian and Carboniferous lavas and sedimentary rocks form the Northeastern Mountains — rugged, dissected terrain, which diminishes in relief towards the Central Lowlands. This region is fringed to the northeast by the Liverpool and Mount Royal Ranges, and by the Barrington Tops, which comprise rugged basaltic terrain of small plateaus interspersed with narrow, steep-sided crests and valleys.

In contrast, the Central Lowlands have a gently undulating terrain developed on easily eroded Permian sedimentary rocks, on which deep soils have developed. The region is, therefore, important agriculturally, but is also important economically for its mineable coal deposits. The Hunter River and its tributaries are bounded by alluvial flats 1–6 km wide.

Rainfall varies markedly with elevation and distance from the coast; the total annual precipitation increases with elevation away from the Central Lowlands, reaching a maximum of about 1500 mm in the higher reaches of the Barrington Tops. Average annual rainfall ranges from 580 mm at Denman in the western part of the study area (Pl. 1) to 1000 mm near the coast. The distribution of rainfall is fairly uniform throughout the year, although monthly means are highly variable, ranging from 50 to 80 per cent.

In the Central Lowlands (Jerrys Plains) average temperatures range from 24°C in summer to 11°C in winter, the yearly average being 17.8°C; in the higher areas frosts are common in winter.

In the Central Lowlands, soil moisture deficits of 10–50 mm per month are frequent from October to March, and little, if any, surplus occurs during the winter period. The southern and northwestern mountains have average annual soil moisture surpluses ranging from 10 to 250 mm, depending on elevation. Base flow of the Hunter River and its major tributary streams is thus very dependent on the physiography and climate of the surrounding highlands.

General geology

The map area incorporates the southwestern tip of the New England Fold Belt and the northwestern half of the Hunter Valley Dome Belt (Fig. 3) (Branagan & others, 1975) in the northern division of the Sydney Basin (Fig. 1). Important works on the evolution and stratigraphy of the Sydney Basin are those of Mayne & others (1974), Branagan & others (1975) and Herbet & Helby (1980). The Permian stratigraphy of the upper Hunter River valley has been described in detail by Britten (1975).

The upper Hunter River valley is underlain by a sequence of alternating shallow marine and continental Permo-Triassic sedimentary rocks, which dip gently ($<10^\circ$) to the southwest and are capped by Tertiary basalt in the north and west (Pl. 1, Table 1); the total thickness of Permo-Triassic rocks is over 4 km. The basement is formed of Late Carboniferous glacigene sedimentary rocks derived from the Lachlan Fold Belt to the south, which are intercalated with volcaniclastics and lava flows from the New England Fold Belt to the north.

In the study area, the northeastern boundary of the Hunter River valley is clearly defined by the Hunter Thrust Fault (Pl.1, Fig.3), which separates the Permian rocks of the valley floor and foot slopes from the northern overthrust Carboniferous rocks in the higher country of the southern New England Fold Belt. The Carboniferous rocks comprise sandstone, conglomerate, and tuff of the lower Carboniferous Gilmore Volcanics and Wallaringa Formation. Remnants and down-faulted



Figure 1. Locality map and generalised surface geology.



Figure 2. Geomorphic subdivisions, Hunter River valley catchment (after Story & others, 1963).

blocks of upper Carboniferous fluvioglacial sediments and volcaniclastics are preserved in some areas.

The western and southern boundaries of the upper Hunter River valley coincide with an escarpment formed by (Lower) Triassic rocks of the Narrabeen Group; these comprise interbedded sandstone and shale overlying basal fanglomerate. The southeastern boundary coincides with the unconformity in the Lochinvar Anticline about 14 km southeast of the map sheet (Fig. 3), where the coal seams and interbedded sediments of the Singleton Super-group wedge out (Britten, 1975).

The major geological structures (Pl. 1) that are hydrogeologically significant consist of a series of meridional faults with numerous associated cross-faults, and doubly plunging folds or domes oblique to the Hunter Thrust Fault. Many of these folds and parallel faults developed contemporaneously with the Hunter Thrust Fault during the mid-Permian Hunter-Bowen Orogeny, and had an important effect on the distribution of Late Permian coal seams and sediments (Herbet & Helby, 1980). The curvilinear traces of the major fold axes (Pl.1) suggest that a minor subsequent phase of folding along an east-trending axis caused buckling of the existing folds and produced the dome and basin structures of the valley. In any event, tectonism had ceased by the time Eocene basalts were extruded in the northern and western parts of the map area. A renewed period of small-scale tectonism associated with Cainozoic uplift is indicated by variations in thickness of alluvium in the upper Hunter River floodplain (Williamson, 1958); these variations in the thickness of alluvium imply that the Mount Ogilvie Fault at the hinge of the valley in the western part of the map area (Pl. 1) was reactivated during the late Cainozoic.

The alternating shallow marine and continental depositional environments during the Permian are shown in Table 1. The Greta and Wittingham Coal Measures formed as peat swamps on alluvial fans close to the sea. Within the Wittingham Coal Measures two brief marine transgressions are recorded by laminites of the Bulga and Denman Formations, which Britten (1975) used to define the tops of the Vane and Jerrys Plains Subgroups respectively. The Wollombi Coal Measures show the least marine influence of the Permian deposits. The coal seams are mostly interbedded with tuffaceous and terrigenous sedimentary rocks. Continental sedimentation continued into the Triassic with the deposition of a basal fanglomerate (Widden Brook Conglomerate) overlain by interbedded sandstone and shale of the Narrabeen Group. No coal seams are present in the Triassic.

Eocene basalts of the Liverpool and Barrington Volcanoes (Wellman & McDougall, 1974) form a prominent planation surface to the north and west of the study area; Galloway (1971) considered that most of the Triassic rocks in the western half of the study area were formerly capped by basalts. Miocene basalts of the Dubbo Province are largely conformable with the contemporary landsurface in the western Goul-



Figure 3. Generalised geology and major structures, Hunter Valley Dome Belt.

burn River valley (Galloway, 1971), indicating uplift and incision of the upper Hunter River valley west of the Mount Ogilvie Fault between the Eocene and Miocene.

The major known Tertiary dolerite sills of the upper Hunter River valley are shown in Plate 1; numerous dyke swarms are not represented, owing to their small areal extent. Most dolerites occur west of a line extending south-southeastwards from the hinge of the Muswellbrook Anticline towards Broke. The dolerite intrusions have in places burnt the coal or converted it to cinders, and thus they have an important influence on the viability of coal exploitation. The present study shows that the line dividing intruded Wittingham coals in the west from essentially non-intruded equivalent units in the east coincides with a differentiation of natural hydrochemistry based on ionic proportions, which suggests that additional unexposed intrusives are present in the western part of the study area.

The only Cainozoic sediments of hydrogeological importance in the map area are the unconsolidated alluvial deposits of the Hunter River floodplain and, to a lesser extent, the alluvial terraces of the major tributary streams. These deposits are generally composed of basal gravels and boulders overlain by an upward-fining sequence of sands, silts, and clays with sporadic shoestring gravels. Secondary pedogenetic pore-filling of the Cainozoic sediments reduces porosity and becomes significant on the oldest (and highest) terraces.

TABLE 1. STRATIGRAPHIC UNITS IN THE UPPER HUNTER RIVER VALLEY

AGE GEOLOGICA MEDIAN THI			OLOGICAL UN DIAN THICKN	IIT AND ESS (m)*		LITHOLOGY		
QUATERNARY	ATERNARY ALLUVIUM			(MU) 14 (MA) 8	(SI) (BR)	Heterogeneous clays, silts, sands and gravels		
TERTIARY	TERTIARY		100	100 (WY)		Olivine basalts Dolerite sills, lacoliths, necks		
EARLY TRIASSIC	NARI	RABEE	N GROUP 200 400	(WY) 350 (MA)	(BR)	Interbedded shales and sandstones on basal fanglomerate		
		Wolld Meas	ombi Coal ures	280 (W 230 (B 340 (D 290 (M 230 (W	VA) R) IC) 1A) VY)	Coal measure sequence with numerous tuff, conglomerate, arenite and claystone interseam beds		
	PERGROUP	asures	Jerrys Plains Subgroup	410 (W 640 (W 340 (B	VY) VA) iR)	Coal measure sequence with 12 major named seams and numerous splits. Fluvial conglomerate, sandstone and claystone interseam beds of irregular thickness terminating in marine laminites (Denman Formation)		
	TON SL	Coal Me	Archerfield Sandstone	10 (M 15 (D	1A) C)	Massive coarse sandstone		
	TA MAITLAND SINGLE	ittingham (Vane Subgroup	80 (W 200 (W 150 (B 250 (D	VY) VA) R) DA)	Coal measure sequence with 7 major named seams. Fluvial sandstone and siltstone interbeds terminating in marine laminated siltstone (Bulga Formation)		
		3	Saltwater Creek Formation	20 (W 40 (B 30 (W 50 (N	VY) (R) VA) MU)	Massive sandstone with basal silty phases		
		Mulb Siltst	ring 250 cone	(SI) 300 (L 140 (N	l) 1A)	Fossiliferous and pyritic shale, siltstone and fine sandstone		
		Muree Sandstone 60 (SI			il)	Pebbly and tillitic sandstone		
		Branx Form	kton 220 (ation 330 (MA) 300 (D DA) 500 (S 520 (L	DC) il) l)	Tillitic sandstone, siltstone and conglomerate		
		Rowa	Rowan Formation		l) /IU)	Sandstone, siltstone, shale and mudstone with intercalated coal seams		
	GRE CO MEAS	Skele	Skeletar Formation 20 (LI) 80 (MU)		.I) ∕IU)	Rhyolite, chert and tuffaceous claystone		
		Farle	y Formation	150 (S	51)	Micaceous sandy siltstone, mudstone, shale, minor limestone		
	V00I	Ruth	erford Formation	400 (S	51)	Conglomeratic sandstone with erratics, mudstone, marl		
	DAL	Allandale Formation Lochinvar Formation > 800 (SI)		51)	Andesitic tuff, breccia, basalt; major shale and conglomerate			
	UNG	Undifferentiated			Acid and crystal tuff, conglomerate (includes glacigene sediments of Seaham Formation)			
CARBONIFEROUS	GRC	Gilm	ore Volcanics			Interbedded tuffs and sandstones		
	-	Wall	aringa Formation			Conglomeratic acid tuffs on basal conglomerate 19/156-1/60		
	*L	ocatior	n key: WY W BR Br	'ybong oke	DC Doyl SI Sing	es Creek Ll Liddell WA Wambo–Bulga leton MU Muswellbrook DA Dartbrook–Aberdeen		

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HYDROGEOLOGY

Previous and current work

Several hydrogeological investigations have been conducted in the study area: Williamson (1958) compiled an inventory of groundwater resources of the alluvial aquifers in the Hunter River floodplain above Denman and in the Dart Brook valley. Griffin (1960) summarised the groundwater resources of the Wollombi Brook catchment in the south, with special reference to alluvial aquifers. Surface water quality of the Hunter River valley has been investigated by Garman (1980). Records of groundwater quality for the past twenty years are maintained by the NSW Water Resources Commission (WRC). Some information on groundwater in the Wittingham Coal Measures is contained in environmental impact statements prepared by the coal-mining companies.

At the time of writing, three major hydrogeological research projects were in progress in the upper Hunter valley: WRC continued to monitor surface water and groundwater quality over the entire Hunter River catchment; the Environmental Geology Subsection of the NSW Geological Survey were researching the hydrochemical characteristics of the Permian rocks in the valley; and the effect of coal mining on groundwater resources in the Permian sequence of the Hunter River valley was being analysed by Australian Groundwater Consultants Pty Ltd on behalf of the NSW Coal Association. The study described in this report was part of a major CSIRO multidisciplinary research program in the upper Hunter River valley.

Regional hydrodynamics

The Hunter River floodplain roughly bisects the study area. The floodplain is a regional groundwater sink for the Permo-Triassic fractured-rock aquifers; bed underflow of the Hunter River represents a dividing streamline for groundwater flow, apart from a few important mixing zones. Contrasts in permeability and porosity between the alluvial and fractured-rock aquifers indicate that most groundwater in the upper Hunter River valley is stored in and transmitted through the floodplain sediments. Multivariate statistical analyses used in this study show that a strong chemical signature from the Carboniferous provenance is maintained through to Singleton in wells of the floodplain that are hydraulically connected to the Hunter River. When these wells are pumped, they are recharged from the Hunter River as their cones of depression intersect saturated sediments peripheral to the river. At the time of sampling (August 1982), withdrawal of groundwater from wells on the floodplain was exceptionally heavy because of prolonged drought.

Several surface reservoirs in the map area act as plane sources for groundwater recharge; they also tend to impede lateral throughflow from upgradient groundwater stores, and in some areas create springs and artesian conditions. The largest reservoir is Lake Liddell (148 000 ML capacity), which is filled with a mixture of water pumped from the Hunter River, runoff, interflow, and groundwater from the 75 km² upper catchment of Baywater Creek. The upper Baywater Creek catchment drains Maitland Group rocks on the eastern limb of the Muswellbrook Anticline. In August 1982, the water chemistry of the lake margin was slightly closer to the mean composition of groundwater of the Hunter floodplain than to groundwater in the Maitland Group rocks.

On a regional scale, groundwater of the fractured-rock aquifers constitutes only a minor proportion of storage and transmission, but the reserves are most important during times of low flow of the Hunter River and its tributaries. However, groundwater in Permian fractured-rock aquifers is very important to the coal-mining industry.

Alluvial aquifers

Basal gravel and overlying sand of the floodplain alluvium of the Hunter River and its major tributaries are by far the most permeable aquifers in the study area. In many places groundwater yields are sufficient to permit intensive crop irrigation (Table 2). In general, wells in floodplains of the Wollombi Brook, Goulburn River, and Hunter River do not extend to bed rock, although more than half the wells in the other tributary valleys listed in Table 2 do.

TABLE 2. MEAN	YIELD AND DEPTH OF WELLS IN TH	ΗE
FLOODPLAIN OF	THE HUNTER RIVER AND MAJOR	
TRIBUTARIES.		

Location	Number	Mean Yield (L/Sec)	Mean Depth (m)		
Hunter River Floodplain					
(Rouchel to	11	191 + 16	11.7 ± 1.0		
(Muswellbrook to	11	10.4 ± 4.0	11.7 - 1.9		
Denman)	12	12.2 ± 6.2	12.5 ± 3.8		
(Denman to Loder					
Creek)	26	12.3 ± 9.6	13.5 ± 2.6		
(Loder Creek to Neotsfield)	25	13.4 + 7.5	143 + 21		
Goulburn River (Sandy Hollow to Hunter River	25	15.4 2 7.5	14.3 = 2.1		
junction)	9	11.9 ± 10.8	14.6 ± 6.3		
Wybong Creek	6	13.5 ± 8.4	13.6 ± 4.9		
Dart Brook	9	8.6 ± 4.8	12.6 ± 3.9		
Martindale Creek	29	12.7 ± 7.9	12.9 ± 2.8		
Wollombi Brook (Broke to Warkworth)	31	8.8 ± 3.4	9.4 ± 4.1		
Milbrodale Brook Hayes, Wambo, North	21	6.9 ± 3.1	6.6 ± 1.9		
Wambo and Appletree Creeks	20	5.8 ± 3.7	7.0 ± 2.6		

Source: (1) WRC boremaster records (2) Griffin (1960)

Fractured-rock aquifers

The permeability of a fractured-rock aquifer depends mainly on the spacing, interconnections, and apertures of the fractures. In an interbedded sequence of coals and more competent rocks, cleats in the coal seams are always more closely spaced than joints formed in competent rocks under the same stress field, because coals store higher strain energy. The ratio of cleat to joint spacing depends on the Young's modulus and Poisson's ratio of the respective rock units; in coals these parameters are related to rank. In addition, fracture spacing is inversely proportional to bed thickness; therefore, under a given regional stress field, the highest frequency of brittle fractures occurs in the coal seams, which are generally thinner than adjacent sandstone and shale interbeds.

The importance of fracture aperture is expressed in the cubic flow law derived by integration of the Navier Stokes equation of laminar flow between parallel planes. This law states that the rate of flux of fluid through a smooth open fracture is proportional to the cube of the fracture aperture. If groundwater that is super-saturated with respect to a particular mineral moves through rock fractures, then that mineral will precipitate in the fracture, provided that the appropriate thermodynamic conditions exist; precipitation commences on the fracture face since the fluid velocity is minimised at the boundary layer, and in time accretes inwards, layer by layer, towards the centre of the fracture or void. Therefore, under conditions of constant effective stress the transmissivity of a fractured-rock aquifer may decline in time if the fractures become lined or filled by precipitated minerals. In the study area most groundwater in the Permian rocks has exceeded calcite, dawsonite, and dolomite saturation, which is consistent with the abundance of healed carbonate fractures in the coal seams and interbedded sedimentary rocks.

The most transmissive fractured-rock aquifers are therefore likely to be those with the most and youngest open tension fractures — the likelihood of lining or filling with mineral precipitates increases with age. Shear planes (conjugate shear joints and faults) are likely to form impermeable barriers to groundwater flow, since displacement is parallel to the plane, but tension fractures oblique to faults may store considerable quantities of groundwater. However, the effective stress of any fractured rock mass is rarely constant for a sustained length of time, and subsequent rotation in principal stress directions may promote jostling along previously tight shear planes and induce displacement oblique to the planes, thereby enhancing the fracture permeability of the rock.

The orientation and location of the youngest tension fractures may be estimated by considering the regional stress history of the upper Hunter River valley since uplift of the Permo-Triassic rocks. The maximum principal stress direction would have been near vertical within a few hundred metres of ground surface, owing to gravitational loading, irrespective of whether initial conditions were hydrostatic or whether there were residual stress components owing to thrusting (Price, 1966). Tension fractures formed under these conditions would have been high-angle sets parallel to the plane of maximum and intermediate principal stress directions. These first-stage tension fractures are clearly visible along the face of the escarpment of Triassic rocks, and conspicuous in the Permian rocks of the Hunter River valley floor as intersecting sets of closely spaced cleats perpendicular to bedding in the coal seams.

Erosional unloading by entrenchment of the Hunter River and its tributaries resulted in rotation of the maximum principal stress, equivalent to the confining pressure of the adjacent rock mass, to a subhorizontal direction, in the eroded section of the valley. The minimum principal stress would have rotated to a vertical direction - approximately orthogonal to the newly formed land surface. A second generation of tension fractures would therefore have developed subparallel to the land surface, but these would have formed only in the lower eroded section of the Hunter River valley, where the unloading effects would have been greatest. In gently dipping rocks, stress relief would have been shown by parting along bedding planes rather than by the formation of new fractures. Consequently, the most permeable fracture sets should be the youngest, low-angle joints and bedding plane separations in the Permian rocks of the valley floor.

The preferential development of closely spaced cleats in coals increases their potential for transmitting groundwater, the bedding plane separations and low-angle tension fractures forming the major conduits. Furthermore, the highest permeabilities within a sequence of coals of equal rank will occur close to the ground surface, because this is where the difference between the maximum and minimum principal stresses is greatest; this stress difference is most pronounced in exhumed coal seams of the Early Permian Greta Coal Measures (Table 1), which were more deeply buried and therefore subjected to greater load stress than the other coal measures.

Several phases of deformation — lateral stretching of uplifted folds and domes (e.g., Muswellbrook Anticline) and slip along the Mount Ogilvie Fault, which was related to early Tertiary igneous activity — were superimposed on structures in the map area. In anticlinal folds, flexural slip-folding about the fold axes produced two sets of primary tension fractures, parallel and perpendicular to the fold axes, whereas, in synclinal folds, the most prominent fractures were conjugate shear joints symmetrical about a plane orthogonal to the fold axis. The hinge areas and limbs of anticlines are therefore generally considered to be the zones of highest fracture permeability, provided that the tension joints have remained open and the rock fabric has not been unduly deformed by cleavage. Subsequent uplift of domal structures may have resulted in further displacement of these tension fractures, owing to lateral extension. Australian Groundwater Consultants (1982) quoted enhanced groundwater yields from fractured rocks of the Muswellbrook Anticline zone.

Tension fracture patterns associated with the dolerite intrusions are almost impossible to predict; within the dolerites, extension cooling joints are commonly symmetrical about the contact zones, but these joint patterns generally do not extend into the surrounding country rock.

Groundwater flow rates

Groundwater velocity is an important constraint in assessing the applicability of equilibrium models in water chemistry to natural conditions. Estimates of regional groundwater velocities for the major lithological units in the upper Hunter River valley (Table 3) are intended only as a guide to relative velocities on a regional scale and are for unconfined flow. In particular, the estimates of velocities in fractured-rock aquifers are likely to be substantially in error on the scale of individual catchments because transmissivity may be highly anisotropic.

TABLE 3. ESTIMATED REGIONAL GROUNDWATER VELOCITY FOR UNCONFINED FLOW IN MAJOR LITHOLOGICAL UNITS OF THE UPPER HUNTER RIVER VALLEY

Unit	Mean hydraulic conduc- tivity	Mean effective porosity	Mean hydraulic gradient	Mean velocity
	(m/day)			(m/day)
Alluvial aquifers in Hunter River floodplain (no pumping)	250 1	0.15	0.0015	2.50
Narrabeen Group	0.01	0.02	0.25	0.13
Wollombi Coal Measures	0.05	0.03	0.05	0.08
Wittingham Coal Measure (west of the Muswellb Anticline)	es rook	0.04	0.03	0.06
Wittingham Coal Measure (east of the Muswellbr	es ook	0.01	0.05	0.00
Anticline)	0.10	0.05	0.02	0.04
Greta Coal Measures and Maitland Group rocks the Muswellbrook	of			
Anticline	0.15	0.05	0.03	0.08
Carboniferous rocks	0.01	0.02	0.20	0.10

Source: AGC, company reports, and WRC records

Calculated results indicate that groundwater velocities in the floodplain alluvium are, at the very least, an order of magnitude higher than in the fractured rocks (Table 3). In addition, the highest velocities in the fractured-rock aquifers occur in the least permeable Narrabeen Group and Carboniferous rocks, where the large hydraulic gradients overshadow the limiting effects of minimal fracture permeability.

The applicability of chemical equilibrium models to the upper Hunter River system may now be assessed in the light of these results. In the Hunter River floodplain the mean contact time between a mineral grain — say 2 mm diameter — and groundwater is about 1 minute; in fractured-rock aquifers mean contact times for similar grain sizes range from about 20 minutes in the Narrabeen Group rocks to over an hour in the Wittingham Coal Measures. Reaction rates for sulphide oxidation and simple dissolution/precipitation in carbonate and sulphate systems are measured in minutes, but silicate dissolution times are normally measured in days; therefore, the use of carbonate equilibrium models would be realistic in the fractured-rock aquifers, but only of limited value in the alluvial aquifers. On a regional scale, the groundwater velocities in all provinces are too high for silicate dissolution/precipitation reaction to be adequately explained by equilibrium models, but this may not necessarily be true on the scale of individual catchments.

HYDROGEOCHEMISTRY

Hydrogeochemical survey and compilation of database

The data (chemical analyses) on which this report is based comprise 673 samples (Pl.2, Appendix 1), of which 340 were collected at the end of a prolonged drought, during August 1982 — 21 from stream base flow and springs, 71 from shallow wells, and 56 from fractured-rock bores — and the remainder are published chemical analyses of groundwater from wells and bores.

Electricity conductivity (EC) was measured in the field with a portable meter, and in the laboratory on a direct-reading digital conductivity meter; pH was measured on unfiltered samples prior to the HCO_{3}^{-} titration.

Prior to analysis for Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Cl^- , SO_4^{2-} , and SiO_2 , the samples were filtered through a 0.45 μ m cellulose nitrate membrane filter, then stored at -20°C. When required for analysis, the filtered samples were thawed, then acidified with nitric acid to a sample concentration of 1% in order to reconstitute the precipitates.

 HCO_3^- was determined by titration; Ca^{2+} , Mg^{2+} , Na^+ , and K^+ , by atomic absorption spectrometry; and Cl^- , SO_4^{2-} , and SiO_2^- colorimetrically, using an auto-analyser; the detection limit for the Cl^- , SO_4^{2-} , and SiO_2^- methods was 0.2 mg/L. An air-acetylene flame was used for the cation determination; strontium chloride, to a final concentration of 1500 mg/L, was added to samples and standards to suppress ionisation. The sensitivities for these determinations were 0.021 mg/L for Ca^{2+} at 422.7 nm, 0.003 mg/L for Mg²⁺ at 285.2 nm, 0.003 mg/L for Na⁺ at 589.0 nm, and 0.01 mg/L for K⁺ at 766.5 nm.

100 samples were analysed by inductively coupled plasma for Al and Fe and the trace elements B, Cu, Mn, Zn, Co, and P; the detection limit was less than 0.01 mg/L for each element.

Correlation and distribution of dissolved salts

TABLE 4. CORRELATION MATRIX OF SIX MAJOR IONS IN UPPER HUNTER RIVER VALLEY GROUNDWATER (n = 670).

HCO ₃	1					
Cl	0.50	1				
SO ₄ ²⁻	0.18	0.51	1			
Ca ²⁺	0.15	0.43	0.65	1		
Mg ²⁺	0.43	0.86	0.72	0.66	1	
Na ⁺	0.62	0.96	0.56	0.35	0.81	1

All correlation coefficients in Table 4 are non-zero at the 95% significance level, and all are positively correlated. The most highly correlated pair of ions (r>0.8) is Na⁺-Cl⁻, followed by Mg²⁺-Cl⁻; both associations give the commutative high correlation Na⁺-Mg²⁺. The lowest correlations (r<0.2) are Ca²⁺-HCO₃ and HCO₃-SO₄²⁻. SiO₂ and K⁺ are not included in Table 4, owing to the large number of missing values for these elements (Appendix 1).

Sampling distributions of the major ions and SiO_2 lumped over the complete data set are all right-skewed; K⁺ showed a lesser conformity. The asymmetrical distributions are partly due to biased sampling, but mainly arise because the ranges of concentrations of elements fall within a lower bound slightly greater than zero set by laboratory detection limits, and an indefinite upper bound dependent upon saturation of the water with respect to a a particular suite of minerals.

Much of the skewness in the HCO₃, Ca²⁺, and SiO₂ distributions (Fig. 4) is removed by transforming the data to \log_{10} class intervals. Although these three distributions actually contradict the hypothesis of log-normality in rigorous goodness-of-fit tests at a level of significance of 0.05, it is quite apparent that they approach unimodal log-normal distributions. This indicates that the concentrations of HCO₃, Ca²⁺, and SiO₂ are the products and not the sums of many small interdependent causes in a statistically homogeneous system; dissolution and precipitation of carbonate and silicate minerals are important influences on HCO₃, Ca²⁺, and SiO₂ concentrations in upper Hunter River valley groundwater, as discussed later.

The polymodal distributions of Cl⁻, SO₄²⁻, Na⁺, and Mg²⁺ (Fig. 4) can be partitioned into discrete modes that individually approach log-normality. Although the effects are again a consequence of the products of many multivariate causes within a particular mode, the sample space can no longer be considered as statistically homogenous. Figure 4 shows that the secondary modes of the Cl⁻, SO₄²⁻, Na⁺, and Mg²⁺ distributions comprise, dominantly, samples from the Vane Subgroup of the lower Wittingham Coal Measures, the Greta Coal Measures, and the Maitland Group rocks; the processes that concentrate these solutes — diffusion of connate marine salts, oxidation of sulphides, and dissolution of evaporite minerals are much more intense in groundwater of these rock types.

Figure 4 shows that K^+ approaches a uniform distribution, implying that there is a mechanism controlling K^+ concentrations that is not operative for other major elements in this system.

Hydrochemical provinces

Groundwater of the upper Hunter River valley has been divided into eight hydrochemical provinces (Table 5, Pl.2). A hydrochemical province is here used to mean a region characterised by groundwater of distinctive chemical composition, stored in and transmitted through particular rock and/or soil associations. Hence, a province comprises a lithological sequence and its associated groundwater, though for convenience in this report it is commonly referred to by the relevant geological term, for example Wollombi Coal Measures, WO (Table 5, Pl.2).

Most CARB province samples in the northeast of the study area are base flow because the mountains of the southern New England Fold Belt are well endowed with surface water and, therefore, very few bores have been drilled. The hydrochemical characteristics described for the CARB group in this report are representative only of a 10 km wide strip of Carboniferous rocks adjacent to the Hunter Thrust Fault; within this zone, recycled salts are introduced from the Permian strata of the valley floor — as shown by proportional increases in HCO_3/CI^- and Ca^{2+}/Na^+ ratios with increased distance from the Permian rocks.

The TRIAS province consists of fractured rocks of the Narrabeen Group. In the northwest of the map area the Triassic



Figure 4. Frequency distribution of anion and cation concentrations in upper Hunter River valley groundwater.

rocks are capped by Tertiary basalt, which is part of an extensive basaltic surface extending westward for almost 100 km. The TRIAS province samples are from shallow wells, base flow, and springs; no boreholes have been drilled in the rocks of the Triassic escarpment because of the ruggedness of the terrain. Groundwater characteristics (Na⁺, Mg²⁺–Cl⁻) for this province are restricted to a 10 km wide zone marginal to the Permian–Triassic boundary, although HCO₃⁻ is present, and even dominant, in groundwater near the Tertiary basalt.

The Permian fractured rocks are subdivided into four hydrochemical provinces: WO, WI1, WI2, and GM. The WO province comprises the Wollombi Coal Measures; ionic proportions in groundwater of these rocks are similar to those of the water of the overlying Narrabeen Group rocks, but mean concentrations are almost twice those in the TRIAS group. The Wittingham Coal Measures are subdivided into the WI1 and WI2 hydrochemical provinces; the boundary between them is a line projected from the hinge of the Muswellbrook Anticline to Broke, and, as noted earlier, this line also divides intruded rocks in the west forming the WI1 province from non-intruded rocks of the WI2 province in the east. In the central part of the valley, the WI1/WI2 boundary follows a 2 km wide buffer zone adjacent to the Maitland Group rocks on the western limb of the Muswellbrook Anticline until it intersects the Hunter River about 5 km southwest of Muswellbrook; northwards to Aberdeen, the WI1/WI2 boundary is defined by the subcrop of the Bayswater seam.

A comparison of the WI1 and WI2 provinces shows several significant differences in environments and groundwater properties: the WI1 province contains scattered Tertiary intrusions; the WI1 province comprises shallowly dipping and relatively undeformed, gently folded rocks, whereas in the WI2 province the rocks dip at higher angles and are extensively folded and faulted, particularly east of the Muswellbrook Anticline; WI1 province rocks are everywhere younger than the Vane Subgroup (Table 1) and, except in the northern area, generally consist of rocks younger than the Mount Arthur seam. Concentrations of total dissolved salts (TDS) in groundwater of the WI2 province for similar residence times and distances down

TABLE 5.	HYDROCHEMICAL	PROVINCES	OF THE	UPPER
HUNTER F	RIVER VALLEY			

Symbol	n	Description	Dominant hydrochemical facies
CARB	33	Carboniferous volcaniclastics and glacigene sediments of the south- ern New England Fold Belt	Na ⁺ , Mg ²⁺ -Cl ⁻ , HCO ₃ ⁻
TRIAS	19	Lower Triassic conglomerate, sandstone, and shale of the Narrabeen Group, overlain in places by Tertiary basalt in the west and south of the area	Na ⁺ , Mg ²⁺ –Cl ⁻
WO	93	Interbedded coal seams and con- tinental sediments of the Wollombi Coal Measures	Na ⁺ , Mg ²⁺ –Cl ⁻ , HCO ₃ ⁻
HFP1	86	Alluvium of the Hunter River flood plain between Glendawn Dam in the north and the Goulburn River confluence	Mg^{2+} , Na ⁺ -HCO ₃ ⁻ , Cl ⁻
HFP2	105	Alluvium of the Hunter River flood plain between the Goulburn River confluence and Singleton	Na ⁺ , Mg ²⁺ -HCO ₃ ⁻ , Cl ⁻
WI1	90	Upper Wittingham Coal Measures west of the Muswellbrook Anticline, in the north, and near the 'Triassic escarpment' in the south	Na ⁺ -Cl ⁻ , HCO ₃ ⁻
WI2	118	Lower Wittingham Coal Measures east of the Muswell- brook Anticline in the north and proximal to Maitland Group rocks in the south	Na ⁺ -Cl ⁻
GM	126	Interbedded coal seams and continental sediments of the Greta Coal Measures, and marine sediments of the Maitland and Dalwood Groups	Na ⁺ , Mg ²⁺ –Cl ⁻ , SO ₄ ²⁻

TABLE 6. SOLUTE CONCENTRATIONS (meq/L) IN UPPER HUN-TER RIVER VALLEY HYDROCHEMICAL PROVINCES.

Province	HCO3		(CĽ		O_{4}^{-}	SiO ₂		
	Ĉ	S	Ĉ	S	Ē	S	Ĉ	S	
CARB	4.62	1.85	6.78	4.57	0.78	0.44	0.24	0.13	
TRIAS	2.92	2.83	6.41	5.73	0.55	0.58	0.20	0.08	
WO	5.00	4.09	11.01	11.63	0.71	1.18	0.46	0.51	
HFP1	5.17	1.69	3.76	3.14	0.64	0.47	0.27	0.24	
HFP2	5.87	2.36	5.73	3.37	0.90	0.64	0.49	0.37	
WI1	11.42	10.89	22.93	22.01	0.99	1.15	0.58	0.81	
WI2	13.98	8.60	68.14	59.62	10.83	8.59	0.26	0.24	
GM	9.41	4.84	40.39	39.84	20.29	25.99	0.27	0.22	
	Са	Ca^{2+}		Mg^{2+}		Na ⁺		<i>K</i> ⁺	
	Ĉ	S	Ē	S	Ĉ	S	Ĉ	S	
CARB	3.05	1.33	3.30	2.12	5.76	3.17	0.07	0.08	
TRIAS	1.64	1.68	3.50	3.30	4.32	2.68	0.14	0.05	
WO	2.38	2.16	4.51	4.74	10.33	10.17	0.21	0.18	
HFP1	2.96	1.52	3.53	1.91	3.14	2.42	0.07	0.11	
HFP2	3.31	1.44	4.16	1.98	5.37	3.12	0.09	0.06	
WII	2.94	2.26	8.83	8.05	25.37	23.93	0.26	0.18	
WI2	5.06	3.70	19.38	15.47	66.78	53.42	0.56	0.60	
GM	10.34	6.77	20.25	16.98	37.40	37.66	0.41	0.36	

flow lines; and the proportion of SO_4^{2-} in anion concentrations is significantly greater in the WI2 province. However, SiO_2 constitutes the most useful solute for distinguishing the Wittingham subprovinces from each other — as discussed later.

An outlier of the WI2 province represented by a line of sporadic salt springs above Big Flat Creek occurs along the surface trace of a diagonal fault that truncates the northern end of the Mount Ogilvie Fault; water from these springs is allocated to the WI2 group by a linear discriminant function.

The GM province incorporates groundwater of the Greta Coal Measures, Maitland Group, and Dalwood Group rocks. This water is distinguished from the WO, WI1, and WI2 groups by its high SO_4^2/Cl^- and SO_4^2/HCO_3^- ratios.

The HFP1 and HFP2 provinces — coincident with the upper and lower reaches respectively of the Hunter River floodplain (Plate 2) — show several differences; increased proportion of CI^- in the anions of the HFP2 province (probably owing to increased contact time with Permian rocks); and diminution in mean grainsize of the aquifers away from the Carboniferous rocks.

Mean and standard deviations of solute concentrations for each of the hydrochemical provinces are shown in Table 6.

Solute behaviour in the hydrochemical provinces

Some fundamental differences in the behaviour of the major elements in groundwater of the hydrochemical provinces are evaluated by means of composition diagrams (Figs. 5-12); more refined analyses using multivariate statistical methods are considered later.

The behaviour of solutes is assessed by regression equations and variables are log-transformed; for example, the equation for Cl⁻ behaviour in the CARB — TRIAS provinces (Fig. 5a) is:

 $\log [Cl] = -0.58 + 1.02 \log [\Sigma \text{ major ions}]$

or [Cl] = 0.263 [Σ major ions] 1.02 — in terms of the untransformed variables.

Regression lines of the hydrochemical provinces are compared to a simple non-evaporative mixing line between the endmembers — standard mean ocean water (SMOW), and mean annual rainfall composition (MUHR) of the upper Hunter River valley (NSWSPCC, personal communication). The MUHR– SMOW mixing line (Figs. 5a, b) defines an upper limit to which all regressions are either subparallel or asymptotic; simple mixing between the MUHR and SMOW end-members seems to explain observed Cl concentrations in this system.

The regression coefficients for each hydrochemical province indicate the mean rate of enrichment of the Y species with respect to a concentration factor (X) within that province. Figure 5a shows that the rate of accretion of Cl^- is highest in the floodplain alluvium, but only over the range of sampled values; a quadratic regression would probably be asymptotic to the MUHR–SMOW line for higher X values, if indeed they exist in the HFP provinces.

The sample space in Figure 5a and b can be partitioned into two environment divisions: the fractured-rock environments (CARB-TRIAS, WO, WI1–2 and GM provinces) and the Hunter River floodplain alluvium (HFP1–2 provinces). The rate of Cl⁻ enrichment in the fractured-rock environments is not significantly different from that of the MUHR–SMOW mixing line, whereas the corresponding rate in the floodplain alluvium is significantly greater. Furthermore, mixing of groundwater in the floodplain alluvium is defined by different end-members: surface water of the Hunter River, which plots around the lower region of the HFP regression line; and groundwater of wells where there is considerable upward and lateral seepage of groundwater from the Permian rocks — these sites are identified later by principal components based on the concentrations of the six major ions. The high correlation coefficients



Figure 5. a,b — Composition diagrams of chloride concentration versus total ions by hydrochemical province.

(Fig. 5a, b) demonstrate the conservative nature of Cl⁻ within the range of concentrations of upper Hunter River valley groundwater; the maximum is still well below halite saturation or any other chloride minerals for that matter. Cl⁻ is therefore the ideal element in this system to use as a standard concentration factor, and the behaviour of all other elements may be compared with it (cf. Eugster & Jones, 1979); in all subsequent composition diagrams Cl⁻ concentration is plotted as X-variable. In HCO₃-Cl⁻ concentration relationships (Figs. 6a, b) there are very few samples in which HCO₃ values could be explained by concentration along flow lines in a linear MUHR-SMOW mixing system. The regression coefficients show that the rate of uptake of HCO₃ is highest in the CARB-TRIAS groups (b=0.65); for the CARB province alone b=0.74. In this group the principal mechanisms responsible for HCO₃ enrichment are carbonate and silicate mineral dissolution. Rates of HCO₃ accretion higher than that for the MUHR-SMOW mixing



Figure 6. a,b — Composition diagrams of bicarbonate versus chloride concentration by hydrochemical province.

system occur in the WO and WI1 province, owing to dissolution of silicates in the dolerite intrusives; in the WO group north of the Goulburn River, an additional source of HCO_3^- is provided by weathering of basalts. A low rate of HCO_3^- enrichment with respect to Cl⁻ occurs in the HFP province (Fig. 6a); this contrasts with the high rate of enrichment of Cl⁻ in the floodplain alluvium mentioned previously. The HFP regression line defines mixing between the two end-members — Hunter River surface water, and groundwater of Permian fractured rocks. A similar low rate of HCO_3^- enrichment occurs in the GM group (Fig. 6b), but this is accompanied by an enrichment in SO_4^{2-} .

 SO_4^{2-} -Cl⁻ concentration relationships (Fig. 7a, b) show that if SO_4^{2-} behaved as a perfectly conserved species, the MUHR– SMOW linear mixing system would be sufficient to account for SO_4^{2-} concentration in all hydrochemical provinces, apart from the GM group. Evidently, other processes of SO_4^{2-} enrichment are present in this group, the most important being oxidation of sulphides, and dissolution of sulphate minerals; however, SO_4^{2-} cannot be regarded as a conservative element, because of its



Figure 7. a,b — Composition diagrams of sulphate versus chloride concentration by hydrochemical province.

tendency to form ion pairs and complexes, and its affinity for surface adsorption on aluminosilicate gels: this is shown by the very low gradient of the CARB–TRIAS regression line (Fig. 7a). In the CARB–TRIAS provinces, aerosols constitute the primary source of both SO_4^{2-} and Cl^- , but much of the SO_4^{2-} is absorbed down flow lines. Some SO_4^{2-} losses are also incurred from H₂S springs in the Wollombi Brook valley section of the WI2 province; therefore, the similarity of the WI2 regression coefficient with the gradient of the MUHR–SMOW line should not necessarily be taken as an indication that the simple process of mixing between meteoric and oceanic water alone accounts for observed SO_4^{2-} concentrations in the WI2 province. A more correct interpretation would be that the WI2 regression coefficient represents the residual rate of SO_4^{2-} enrichment, which is controlled by the combined effects of flushing of connate marine salts by meteoric water, sulphide oxidation, and sulphate mineral dissolution — less the effects of sulphate reduction, adsorption, and possibly precipitation.

Cl⁻-normalised SO₄²⁻ concentration relationships (Fig. 7c, d) show that, in the WO and WI1 provinces, samples with very low, constant SO₄²⁻ concentration, but with increasing Cl⁻ concentration, are defined by the line, $\log(SO_4^2/Cl^-) = -1 - \log(Cl^-)$: these points mainly consist of base-flow samples in streams with a substantial part of their catchments in the







Figure 7. c,d — Composition diagrams of normalised sulphate versus chloride concentration by hydrochemical province.

Triassic rocks. The concentration clusters outlined in Figure 7c and d mostly represent groundwater from shallow wells, whereas samples with the highest SO_4^{2-}/Cl^{-} ratios — in the WI1 and WO provinces — are from bores in fractured rocks and deep wells that bottom on bedrock. The clusters of shallow

well concentrations can therefore be considered as mixing zones between the two end-members: interflow/surface runoff from the Triassic rocks; and deeper water from fractured rocks within the same province. In addition, Figure 7c shows that the mean rate of change of the SO_4^{2-}/Cl^{-} ratio is highest in the



Figure 8. a,b - Composition diagrams of silica versus chloride concentration by hydrochemical province.

Hunter River floodplain alluvium; when compared with Figures 5a and 7a, this high rate of change reflects the higher than average increase in the rate of Cl⁻ enrichment in the HFP provinces.

The behaviour of SiO₂ relative to Cl⁻ (Fig. 8a, b) is probably the most useful method of differentiating between the individual Permian hydrochemical provinces. SiO₂ concentration increases sympathetically with Cl^- in the WO and WI1 groups, but decreases with increasing Cl^- in the WI2 and GM provinces. The decline in SiO₂ with increased salinity (TDS) in the latter groups is not due to precipitation of amorphous silica or silicate minerals such as sepiolite, since most WI2 and GM water is undersaturated with respect to these minerals. Rather, it represents precipitation of aluminosilicates, dominantly



Figure 9. a,b — Composition diagrams of calcium versus chloride concentration by hydrochemical province.

montmorillonite, with a concurrent progressive decline in silica solubility in the alkaline Cl-rich solutions of the WI2 and GM provinces.

The M–D–JP triangle curves (Fig. 8a, b) describe high SiO₂enrichment rates in wells and bores within and adjacent to a triangle with apices at Muswellbrook (M), Denman (D), and Jerrys Plains (JP); these samples are all saturated with respect to amorphous silica and sepiolite, presumably because of the numerous local dolerite intrusions which generated the high SiO₂ background. Analyses of well water in the Hunter River floodplain at Alcheringa form a distinct cluster enriched in SiO_2 (Fig. 8a); further on it will be shown that the principal components based on the major ions alone indicate that the locality is an important mixing zone between groundwater of the alluvium and the underlying Wittingham Coal Measures.

The relationships of Cl^- to Ca^{2+} , Mg^{2+} and Na^+ concentrations (Figs. 9, 10, 11) show that the sources of the divalent cations must be other than by mixing of meteoric and oceanic water — as indicated by comparisons of the regression lines with the the MUHR–SMOW mixing lines; however, the MUHR–SMOW mixing system could explain the Na⁺ concentration in about half of the samples (Fig. 11a, b).



Figure 10. a,b — Composition diagrams of magnesium versus chloride concentration by hydrochemical province.

The diversity of sources of the major cations in the recharge zones is related to their total variance at low Cl⁻ concentrations: Ca^{2+} has the greatest dispersion of data points (Fig. 9a, b), and hence the greatest diversity of sources; Mg^{2+} has a lower variance (Fig. 10a, b) and, therefore, a more restricted number of sources; and Na⁺ has the lowest variance (Fig. 11a, b) and least number of sources. Silicate mineral dissolution is an important source of these cations (Ca⁺, Mg²⁺, Na⁺), but dissolution of carbonate minerals is also a prominent source of Ca^{2+} , and probably even provides small amounts of Mg^{2+} .

Comparison of regression coefficients (Figs. 9, 10, 11) indicates that Ca^{2+} has the lowest rate of enrichment of the three cations, despite having the greatest diversity of sources.

In low-salinity groundwater the principal mechanism of Ca²⁺-depletion is probably cation exchange; in the Permian rocks, Ca²⁺ is lost by precipitation of calcite and other carbonates. Again, the composition diagrams for the divalent cations segregate the HFP provinces (Figs. 9a, 10a) on the basis of unusually low rates of Ca²⁺ and Mg²⁺ enrichment.

Figure 11 (a, b) shows that Na^+ is the most conservative of the cations. The rate of Na-enrichment in the CARB–TRIAS, HFP, and WO provinces is significantly lower than the MUHR–SMOW mixing system. Given that these groups have never been trangressed by ocean water, the rates of Na⁺ enrichment shown by their regression coefficients probably reflect dissolution of sodium silicates. However, flushing and



Figure 11. a,b — Composition diagrams of sodium versus chloride concentration by hydrochemical province.

mixing of connate marine salts by meteoric water could account for the Na^+ concentration in the majority of samples in the WI1, WI2 and GM provinces (Fig. 11b).

The behaviour of K^+ (Fig. 12a, b) is quite different from the other major cations. The correlation between K^+ and Cl⁻ concentrations in the HFP and CARB–TRIAS provinces is not significantly different from zero, owing to the resistance to weathering of sanidine and muscovite in the CARB rocks, and the permanent incorporation of K^+ present in circulating groundwater into clay lattices. The apparently random behaviour of K^+ concentration in HFP provinces (Fig. 12a), which is reflected in the almost uniform K^+ distribution (Fig.

4)) over the total sample space, is partly the result of the application of fertilizer to the floodplain soils. In contrast, the rate of K^+ enrichment in groundwater of the Permian rocks is significantly greater than zero; the coal measures may have been an important source of K^+ .

Mineralogy and geochemistry

Framework grains in the Permo-Triassic sedimentary rocks of the upper Hunter River valley are dominantly quartz, feldspar, and volcanogenic rock fragments; however, cements and authigenic minerals yield some important information on



Figure 12. a,b — Composition diagrams of potassium versus chloride concentration by hydrochemical province.

hydrochemical systems, and knowledge of the paragenesis of these constituents facilitates evaluation of the present and palaeohydrogeochemical regimes.

In the Permian rocks, carbonates are the most abundant cement and replacement minerals, whereas in the Lower Triassic rocks, silica and clay minerals are co-dominant with carbonates in the rock matrix.

The most common carbonate mineral is calcite (CaCO₃), which occurs as a cement, replacement mineral, and graincutan material in both marine and continental sedimentary rocks. In the Permian coal seams calcite invariably lines cleat faces, and fills numerous subsidiary joints and veins; in some high vitrinite coals there has been substantial replacement of coal by calcite (Kemezys & Taylor, 1964). Calcite frequently replaces sodic plagioclase and rock fragments in the Permian sediments and feldspars and pyroxene in dolerite intrusions (Mayne & others, 1974). Complete replacement of claystone bands by fibrous calcite exhibiting fine-scale cone-in-cone structure has been described in the Liddell area by Bunny (1967).

Siderite (FeCO₃) is widely distributed as a microcrystalline cement throughout the Wittingham and Wollombi Coal Measures, but occurs mainly in thin beds and lenses of concentrically zoned nodules within the coal seam (Kemezys &

Taylor, 1964); siderite nodules tend to occur to the exclusion of pyrite and are most abundant in coal seams that are not overlain by marine rocks.

Pure dolomite $(CaMg(CO_3)_2)$ is rare in the non-marine rocks in the upper Hunter River valley area (Kemezys & Taylor, 1964), because there is generally some Fe substitution for Mg to form the mineral ankerite $(Ca(Fe,Mg)(CO_3)_2)$. The mode of occurrence of ankerite and dolomite is identical to that of calcite, and like calcite and other complex carbonates, ankerite and dolomite are considered to be of recent origin in coals distant from marine rocks; an exception occurs in some coal seams proximal to marine sediments, where dolomitic lenses replacing clays appear to have formed during early diagenesis.

Dawsonite (NaAl(CO₃)(OH)₂) is particularly interesting, because its formation ranges from very early diagenesis to the present. It is ubiquitous throughout the Permo-Triassic sedimentary sequence of the upper Hunter River valley area and reaches a maximum concentration in the Middle Permian rocks. Dawsonite occurs as geologically recent precipitation on cleat faces, cements, replacement minerals, and joint and vein fillings: in the Mulbring Siltstone (Table 1) it forms spherulites in dolomitic lenses (Loughnan & Goldbery, 1972). In some places the spherulites are replaced by calcite and kaolinite, which are incipiently altered to nordstrandite (Al(OH)3 - a polymorph of gibbsite) around aggregate margins (Loughnan & Goldbery, 1972). Precipitation of dawsonite requires high pH values in sodic solutions enriched in Al relative to Si. These conditions are commonly satisfied in the present groundwater of many of the Permian fractured rocks (see Appendix 1), and apparently have always been present throughout the evolution of upper Hunter River valley groundwater.

Primary and authigenic sulphate minerals are relatively sparse in the upper Hunter River valley aquifers and are mostly confined to the Permian rocks earlier than the Wittingham Coal Measures. Acicular gypsum crystals occur on joint and cleat faces in the Greta Coal Measures and are formed by the reaction of Ca-carbonate minerals and acids released from sulphide oxidation. The former abundance of primary sulphate minerals is recorded by glendonites in the Mulbring Siltstone: glendonites are stellate aggregates of euhedral crystals which, in the upper Hunter River valley area, are mostly composed of calcite pseudomorphs after glauberite (Na₂ Ca(SO₄)₂); Loughnan & Goldbery (1972) also described less-common dolomite, gypsum (CaSO₄.2H₂O) and dawsonite pseudomorphs, and Conybeare & Crook (1968) described glendonites in the equivalent Ulladulla Mudstone in the southern Sydney Basin as siderite pseudomorphs after glauberite. However, the nature of the primary mineral in glendonites is controversial. Australian literature on glendonites in the Sydney Basin has always cited glauberite as the primary mineral - in keeping with the definitive work by David & others (1905) - whereas Kemper & Schmitz (1975) concluded that thenardite (Na₂SO₄) was most likely the primary mineral. In any event, the genesis of glendonites is not in doubt: they form below the surface of marine muds in marginal basins or embayments characterised by dense highly saline water in which there is restricted mixing with the open sea (Conybeare & Crook, 1968). Glauberite precipitates in super-chilled solutions below 0°C, but Kemper & Schmitz (1975) concluded that under specific conditions thenardite glendonites also form at these very low temperatures as indicated by their contemporary formation in semiisolated polar marine basins such as the White Sea.

Sulphide minerals occur in every Permian coal seam and marine sediment in the upper Hunter River valley area, but their distribution is highly variable; we are not aware of any reported occurrences of sulphides in the Triassic or Carboniferous rocks. In the Permian rocks, sulphides are most abundant in the Greta Coal Measures, Maitland Group, and the Vane Subgroup and Denman Formation of the Wittingham Coal Measures. Pyrite is the dominant sulphide — especially in coal seams adjacent to marine beds — followed by marcasite (FeS_2) and accessory sphalerite ((Zn,Fe)S). Arsenopyrite (FeAsS) has been reported in a well-mineralised sandstone below the Bayswater seam at Saxonvale (Croft & Associates, 1979).

The mode of occurrence of pyrite ranges from infilled celllumens and mineral replacements in vitrinite coals, to small spherical nodules that coat bedding planes at coal-band interfaces, through to interlocking mosaics of anhedral crystals; concentrations of massive euhedral crystals at the top of the Greta Coal Measures impart the 'brassy tops' characteristic for which these coals are renowned (Kemezys & Taylor, 1964). Sulphide content in the coals is closely correlated with total sulphur content; from sulphur isotope fractionation studies, Smith & Batts (1974) concluded that much of the pyritic sulphur in the upper seams of the Greta Coal Measures formed by reduction of marine sulphate that diffused downwards into the system during the transgressive phase of the Maitland Group sediments. They also concluded that diffusion of marine sulphate into the Greta coals occurred while the biogenic mass was still active; sulphide enrichment involved the direct reaction of oceanic sulphates with organic compounds and precipitation by sulphate-reducing bacteria. On a smaller scale, it appears that the biomass in the peat which formed the Wynn seam of the Vane Subgroup was apparently reactive during marine transgression and deposition of the overlying Bulga Formation.

A strong link between total sulphur and the proximity of marine sediments (Fig. 13) is clearly shown in the coal seams of the Wittingham and Greta Coal Measures in the Mount Arthur and Saxonvale areas; unfortunately, a composite section for the entire Permian coal sequence is not available at present. Trends in SO_4^{2-} and Cl⁻ concentrations of oxidised coal extracts from the Jerrys Plains Subgroup at Saxonvale (Fig. 13) indicate that, in the Wollombi Brook valley, a similar enrichment in sulphide probably occurred in the Whybrow seam underlying the Denman Formation (the final marine transgression); however, this trend is not apparent in the Mount Arthur area.

In the contemporary hydrochemical environment of the upper Hunter River valley area, sulphides are readily oxidised to sulphates in near-surface groundwater. The upper endmember of the GM province mixing system (Fig. 7b) is enriched in SO_4^{2-} relative to seawater. This enrichment can be explained by the sieving of preferential biogenic sulphate from seawater, resulting in enrichment of sulphides by reactive peats before the onset of coalification; in the present oxidising environment these initially high sulphide concentrations are being returned to the leaching groundwater system as sulphates. A similar explanation can be applied to the highsulphate groundwater of the Vane Subgroup of the WI2 province (Fig. 7b). At the other end of the scale, the equivalent end-member in the WO mixing system (Fig. 7a) is the continental sulphate store in the original Wollombi peat swamps, because these sediments have never been inundated by seawater. Average total sulphur in the Wollombi coals ranges from 0.3% to 0.5% and is mostly organically bound; there are no pronounced vertical concentration gradients typical of the older Permian coals.

Although carbonates and sulphur-bearing minerals constitute the main authigenic minerals of hydrochemical importance in the study area, silica and certain phyllosilicate minerals have an important influence on the chemistry of local groundwater within individual catchments, and particularly in areas containing basic igneous intrusions. The most common form of authigenic silica in the Permian rocks is chalcedony, which appears to have crystallised mainly from globular masses of amorphous silica (Kemezys & Taylor, 1964) in lenses essentially conformable with bedding, and in cell cavity fillings. Vein chalcedony in coal seams occurs most frequently in areas adjacent to igneous intrusions, and it is concluded that



Figure 13. Variation in sulphur, sulphate, and chloride content of coal seams from the Wittingham and Greta Coal Measures.

these occurrences are genetically related to the intrusions. Kaolinite (Al₂Si₂O₅(OH)₄) is the most abundant authigenic silicate in the coal seams. Kemezys & Taylor (1964) described extensive kaolinite petrifactions composed of uncollapsed coalified plant cell walls filled with finely crystalline kaolinite. In the interseam beds, kaolinite, illite-montmorillonite (KAl₂(AlSi₃)O₁₀(OH)₂-Na_{0.33}(Al_{1.67}Mg_{0.33})Si₄O₁₀(OH)₂), and chlorite (Mg₅Al₂Si₃O₁₀(OH)₈) occur extensively as weathering products and primary matrix materials. Kaolinite and illitemontmorillonite are the dominant minerals in claystones that occur intermittently throughout the Wittingham and Wollombi Coal Measures. Some of these layers are derived from in-situ weathering of ash-fall tuffs (e.g., Fairford Claystone); others are detrital in origin. Analcite (NaAlSi₂O₆.H₂O) forms up to 35 per cent of the volume of sediments in the Newcastle Coal Measures (Loughnan, 1966), which are the eastern equivalent of the Wollombi Coal Measures. The mineralogy of these coal measures is virtually unknown because the Wollombi coals have not been exploited, having a high content of tuffaceous material, which makes them sub-economic. The analcite deposits in the Newcastle Coal Measures formed by devitrification of volcanic glasses in tuffaceous sediments under a highly alkaline and Na-enriched groundwater regime. Therefore, zeolites, such as analcite, are probably also present in appreciable quantities in the tuffaceous interbeds of the Wollombi Coal Measures.

In the upper Hunter River valley the most detailed geochemical studies are of the coal seams and interbeds of the Jerrys Plain Subgroup at Saxonvale, and at Mount Thorley in the Wollombi Brook valley (Croft & Associates 1979, 1981). In general, the non-marine interseam beds have a low salinity status (mean TDS less than 1500 mg/L), and HCO₃ is the dominant anion; conversely, the coal seams have an average TDS concentration of 5000 mg/L, and Cl- is the dominant anion, exceeding HCO_3^- concentrations by an average of 15:1. Groundwater composition reflects the variation in soluble salt concentration; piezometers set at varying depths invariably encounter the most saline groundwater in the coal seams, which are also the major aquifers in the Permian fractured rocks. Saline groundwater in the Denman and Bulga Formations (Table 1) and in the Mulbring Siltstone also has high Cland SO_4^{2-} concentrations, although the permeability of these rocks is at least an order of magnitude lower than that of the coal seams. As there are no primary chloride minerals in the Wittingham Coal Measures, the chemical composition of groundwater in the coal seams can only be explained by a significant input of marine salts, either by direct infiltration into peat during marine transgression or by subsequent translocation of connate marine salts during diagenesis.

An interesting result of the Saxonvale and Mount Thorley studies is that the coarse-grained rocks most closely associated with high-energy fluvial depositional environments (lithic sandstones and conglomerates) have consistently higher soluble salt concentrations (mainly NaCl) than the finer grained interseam siltstones and mudstones. The coarse-grained rocks form secondary salt stores, because, in contrast to the argillaceous sediments, they have greater void space, which is filled with connate marine salts in fluids expelled from adjacent coal seams; conversely, these reservoir rocks would also leach at a much faster rate under appropriate conditions. The initial expulsion of connate fluids would have resulted from the volume reduction caused by coalification processes, the effects being most marked in sediments adjacent to the coal seams, which were originally porous peat deposits saturated with marine water and salts. Modern processes that transmit connate marine salts include molecular diffusion driven by concentration gradients, and upward convection and dispersion of water from the semi-confined coal seams in response to differences in groundwater potential. However, the quantity of solutes transferred by these processes in the present groundwater

regime is minor in comparison to the historical expulsion of connate fluids from the original peat deposits during burial and coalification; the transition from peat to bituminous coal represents a porosity decrease from over 80% to between 5% and 10%.

Salt efflorescences

During the severe drought conditions of August 1982, banks and low terraces in the lower reaches of almost every minor stream draining the WI2 and GM provinces were coated by surface salt encrustations (efflorescences); bulk mineralogy of some efflorescence samples was determined by X-ray diffraction (Table 7) — the semi-quantitative ranking of mineral proportions is based on adjusted diffraction peak areas: *major* indicates that a particular mineral is most abundant regardless of its absolute percentage, and *two or more major* minerals indicate that they are present in approximately equal amounts; *minor* indicates that the mineral constitutes more than about 10% of the sample, but is present in significantly lower amounts than the major mineral(s); and *trace* indicates amounts less than roughly 10% of the bulk samples.

Halite is the dominant mineral in salt encrustations (Table 7) and occurs in drainage lines and salt springs in the WI2 and GM provinces. It is also prominent in planar void infills resulting from contemporary wetting and drying of the subsola in soils near salt-affected areas; halite crystals also coat ped faces in the lower B horizon of these soils. Invariably, there is a secondary diffuse layer (halite) around the root zone, but the older concretionary, tubular and macro-cutanic pedological structures do not contain halite. Thus redistribution of halite into the unsaturated zone appears to be comparatively recent.

The sulphate minerals thenardite and bloedite are subordinate to halite in the WI2 and GM provinces, and gypsum was found only in salt efflorescences in the GM province.

In contrast to their abundance in precipitates in the saturated zone, carbonate minerals are not important constituents of salt efflorescence, owing to the lower CO_2 partial pressures in the unsaturated zone, which promote carbonate precipitation before groundwater reaches the surface; this results in an enrichment of Na⁺, Cl⁻, and SO₄²⁻ in groundwater in the unsaturated zone: the abundance of concretionary carbonates in the soils of the Central Lowlands (Fig. 2) supports this argument.

Two main categories of salt efflorescence are present in the upper Hunter River valley area. The first and most spectacular of these comprises salt crusts up to several centimetres thick, which are formed by evaporative concentration of stream water, springs, and seepages in the GM and WI2 provinces of the Central Lowlands. Most salt efflorescences occur in the Wollombi Brook valley between Broke and Singleton. The Mulbring Siltstone, in particular, generates a large number of salt scalds and salt-affected streams. Salinisation of soils, streams and groundwater in the Central Lowlands is closely related to rock type, and the intensity of halite salting is greatest in provinces where groundwater has the strongest connate-marine signature. Some point sources of natural salt contamination existed before European settlement in the Central Lowlands or were contemporaneous with it, as evidenced by early geographic names with salinity connotations - such as Saltwater Creek. Forest clearing has undoubtedly exacerbated degradation of the land by promoting salting under conditions of increased runoff, erosion and rising water tables in the Central Lowlands.

The second category of salt efflorescence in the upper Hunter River valley appears to be controlled in part by geological and geomorphological features. The efflorescences consist of small-scale salt scalds extending downstream from ephemeral springs along the nick point separating the upper and lower pediments on the northeastern and southern sides of the

TABLE 7. MINERALOGY OF SALT EFFLORESCENCES, UPPER HUNTER RIVER VALLEY.

Sample	Location	Mineralogy			
site (Plate 2)			Major	Minor	Trace
46	Fordwich Creek	Surface encrustation on sand terrace. Nodules in B horizon of grey solodic. Crystallaria in lower B horizon.	H D,Q H	C,F	D
48	Fordwich Creek	Surface encrustation on stream bank. Nodules in lower B horizon of solodic. Joint plane infills in lower B horizon.	H H,Q	F	T C
51	Salt Pan Flat	Surface encrustation on alluvial flats. Infill in bedding plane separation, laminated siltstone (Denman Fm?).	H,B,Q H,T,I-M	T K	К
54	Loder Creek	Surface encrustation on sand. Precipitate from subsolum seepages of buried soil. Nodules in subsolum of buried soil. Soluble salts in B horizon of buried soil.	H H D,Q H		T D,Q F
55	Loder Creek	Surface encrustation on sand. Carbonate joint infills in fine sandstone.	H D,Q	F	
56	The Salt Flats	Surface encrustation on outwash sand.	H,T	В	
64	Loder Creek (east arm)	Salt spring efflorescence crust.	H,T,B	Q	
66	Doughboy Hollow Creek	Surface encrustation on low terrace.	Н	T,B	G,I,K,
67	Abbey Green Creek	Surface encrustation on sand.	Н,Т,	Q	
127	Spurwater Creek	Surface encrustation on stream banks.	H,G,B	Q	F
129	Coalhole Creek	Surface encrustation on banks. Efflorescences in sandstone joints. Crystallaria in brown earth.	H H C,Q	F	F
135	Swamp Creek	Surface encrustation on banks. Precipitate from spoil heap. Nodules and joint plane infills from lower B horizon or podzolic	H H,Q .H,D	T,B F Q,F	T,D I,K
171	Rixs Creek	Joint plane infills and macrocutans in subsolum of brown podzolic Tubules in lower B horizon of brown podzolic. Carbonate lenses in sandstone.	.C,Q Q D	F	F,M C Q
180	Drayton	Salt encrustation on casing of artesian bore.	H,G	B,T	Ch,K,M
308	Vere	Soluble salts in pallid zone of deep weathering profile.	Н		D

Mineral abbreviations: B, bloedite; C, calcite; Ch, chlorite; D, dolomite; F, feldspar; G, gypsum; H, halite; I, illite; I-M, interstratified illite and montmorillonite; K, kaolinite; M, montmorillonite; Q, quartz; T, thenardite.

Hunter River valley. Salt crusts in these areas comprise patchy impure films, 1 mm to 2 mm thick, which drape tunnelled dispersive clays. Most springs at the head of the salt scalds on the northeastern side of the Hunter River valley - between Bowmans Creek and the headwaters of Bettys Creek - are roughly coincident with the Hunter Thrust Fault and probably represent saline water upwelling from the underlying Wittingham Coal Measures. However, similar springs on the western footslopes of Mount Surprise, and in the hills above Muscle and Grasstree Creeks occur in Carboniferous rocks at least 3 km from the Hunter Thrust Fault. Most salt scalds at the change of slope on the southern side of the valley between Alcheringa and Bulga seem to emanate from intermittent saline springs at the contact between the Wollombi and Wittingham Coal Measures. In August 1982, despite the drought, one of these springs was still flowing from the base of the Watts Sandstone (lowest member of the Wollombi Coal Measures) above Appletree Creek. Other salt scalds in this area appear to be related to springs and seepages at the contact between the basal fanglomerate of the Narrabeen Group and the underlying Wollombi Coal Measures.

The physical controls on this second category of salting in the upper Hunter River valley area are unresolved, and the chemical composition of the precipitates is not known. However, many of the southern salt efflorescences seem to be closely linked to saline springs from the Denman Formation; others appear to be related to flushing of secondary salts from porous coarse-grained rocks. The connection between the Hunter Thrust Fault and the ephemeral springs and salt scalds on the northeastern side of the valley is tenuous, because there are too many examples of salting unconnected with the fault zone. Alternatively, the salt efflorescences may represent the position of maximum fluctuation of the capillary fringe induced by a combined contrast in soil and rock permeability, coincident with the change in slope of the land surface. A decrease in soil permeability arises from the onlap of open colluvium in the subsola of the fan soils against the older podzolic soils of the lower pediment, where more advanced pedogenesis has resulted in a higher degree of secondary pore filling in the subsola. This is also an area where permeability changes in the underlying fractured rock, since it is the transition zone between a horizontal maximum principal stress direction in the rocks of the central valley section and a vertical principal stress direction in the rocks of the elevated areas.

Minor elements

Analyses of B, Cu, Mn, Zn, Mo, Co, P, Fe, and Al for 100 upper Hunter River valley groundwater samples (Appendix 2) show that group mean concentrations of Cu, Mn, Zn, Mo, Co, and Fe are not significantly different from zero, but that the variances of Mn, Zn and Fe concentrations are high because of anomalous high counts in outliers of groundwater of the



Figure 14. Means and ninety-five per cent confidence intervals for B, P, and Al concentration by hydrochemical province. Permian fractured rocks; Cu, Mo, and Co concentrations are uniformly low throughout the eight hydrochemical provinces. Means and 95% confidence intervals for the significant trace elements B, P, and Al are shown for each province in Figure 14. Within the Permian fractured rocks there is a trend for these elements to be minimised in the WO province and maximised in the GM province. More specifically, mean concentrations of B, P, and Al are significantly higher in the GM province than in any other province, but there is no significant difference between mean concentrations in the WO and WI provinces.

Boron content in Permian coals and interseam beds has been used as a palaeo-environmental indicator by Swaine (1962, 1971), and his results are reproduced in part in Figure 14 for comparison with dissolved B in upper Hunter River valley groundwater. Swaine (1962) regarded seawater as the primary source of B in the Permian sediments, and concluded that the Greta Coal Measures were marine-influenced, the Tomago Coal Measures (Wittingham correlatives) were influenced by brackish or intermittent marine conditions, and that the Newcastle Coal Measures (Wollombi correlatives) were freshwater deposits. In a subsequent study of Bowen Basin coals Swaine (1971) stipulated that differences in boron content only become significant if marine transgression occurred during the very early stages of coalification, which allowed uptake of B by organic matter; this is consistent with conclusions drawn from the sulphur isotope study of Smith & Batts (1974). The trend established by Swaine (1962) for the Permian coals is reflected in the B concentration of their groundwater (Fig. 14). The most likely source of B in CARB-TRIAS province groundwater is dissolution of minerals such as tourmaline; in HFP province groundwater, B probably represents a composite derived from all the other provinces.

Phosphorus level in groundwater is generally considered to be high when the concentration exceeds about 0.2 ppm; Figure 14 shows that most upper Hunter River valley groundwater falls into this category. A significant proportion of phosphorus in groundwater of the Permian Coals probably represents initial fixation of organic collophanes in the peat swamps, but the trend of increasing P with increasing degree of marine influence (Fig. 14) suggests a second source, involving dissolution of phosphate minerals formed in marine mud of estuaries and embayments. The comparatively high P concentration (0.4 ppm) in the TRIAS province may be partly derived from phosphatic nodules in the Narrabeen Group described by Mayne & others (1974), whereas the source of P in the CARB province is more likely to be dissolution of primary phosphate minerals of the apatite group. A proportion of the phosphorus content in HFP province groundwater may be derived from modern applications of phosphate fertiliser in the irrigation areas

Aluminium concentrations (Fig. 14) probably comprise a substantial proportion of particulate gibbsite or aluminosilicates, because samples were filtered only to $+0.45 \mu$ m; Hem (1970) described Al determinations from samples inflated by gibbsite crystals of 0.10 μ m diameter, which easily pass through the standard laboratory filters. Al solubility is highest in acid water and Hem (1970) quoted Al concentrations of several hundred ppm in water of pH less than 4. Therefore, the Permian acid peat swamps would have been an important sink for Al, which could have attained quite high concentration as alumina gel. Al concentration in groundwater of the Permian fractured rocks is roughly proportional to the abundance of the alumino-carbonate mineral, dawsonite, in the aquifers.

Base flow in the upper Hunter River valley area

The groundwater sampling program was undertaken during August 1982, near the end of a prolonged drought; the last significant rainfall to recharge the groundwater store before the drought was in March 1981. The drought conditions therefore presented a unique opportunity for investigating base-flow chemistry and identifying the main sources of groundwater salinity; there was no rainfall during the period of sampling.

At the time of sampling, very few minor streams in the upper Hunter River valley area were flowing, and base-flow samples for these streams - comprising bed underflow water - were taken from depths ranging up to 2 m below the base of the stream bed. A piezometer of perforated PVC casing was jetted into the sands of the stream bed and then pumped intermittently until the electrical conductivity (EC) of the pumped water had attained a constant value (+10%) over at least two consecutive pumping cycles. In most cases the requirement of constant salinity in bed underflow water over the final two pumping cycles necessitated an average of five cycles of alternating drawdown and recovery spread over a couple of days; for this reason, most variations in base-flow chemistry covered a period of more than one day. The constraint on suitability of sites for grab samples in flowing streams was that the lateral variation in EC across the stream should not exceed 10%.

Initially, attempts were made to measure longitudinal variations in base-flow chemistry in every stream contained within and draining into the Denman–Singleton–Muswellbrook triangle, particularly across geological and structural boundaries. However, in some minor streams this objective was hindered by the following factors:

- generally no bed underflow water was intercepted within 2 m of the base of clay-bottomed streams (e.g. Farrells Creek);
- the requirement of constant salinity over at least two pumping cycles could not be attained within reasonable time (e.g., Whites Creek);
- disturbance to natural drainage by engineering works and restricted access (e.g., Mount Arthur, Howick, and Saltwater Creek areas).

Base-flow sampling was prematurely terminated by rains at the end of August 1982. Longitudinal variation in concentration of the major ions in base-flow of the upper Hunter River and its tributaries is shown in Figures 15 to 20, and sample locations, in Plate 2.

In flowing streams, the locus for each ionic species between sampling points is controlled to some extent by ionic composition estimated from intervening EC measurements; however, there is no similar control in the bed underflow water. The frequency of grab samples in the flowing streams was lowest along those sections where variation in EC measurements was small, and highest where large fluctuations were recorded. Changes in composition in response to mixing between two streams - schematically represented in Figures 15 to 20 — were calculated by proportion from known initial and thoroughly mixed concentration values, and estimated stream discharges; the loci of ion concentrations at and immediately below stream junctions represent the average value across the main stream, which is not necessarily the same as the concentration at the centre line. Where the base-flow chemistry of the tributary stream was not greatly different from that of the main stream, the average concentration across the main stream after mixing was approximately equal to the centre-line concentration locus (e.g., Goulburn River-Wybong Creek). However, where stream salinities were very different (e.g. Wybong Creek-Big Flat Creek), EC traversing showed that the saline tributary plumes were not thoroughly dispersed into the main streams for 1 to 2 km downstream from the confluences. In such cases, the schematic loci of ion concentrations were quite different from actual concentrations along the centre line of the main stream.

Salinity variation in the major streams of the upper Hunter River valley during August 1982 is shown in Figure 15 (measurements taken in previous years over a range of flow conditions were documented by Garman, 1980.) The Hunter River is the only stream in the valley where variation in water chemistry could not be solely attributed to groundwater influences, because the flow of the river was regulated by the addition of water from Glenbawn Dam. From Rouchel to upstream of Denman there was a small but steady increase in salinity; Cl⁻ and HCO₃ increased at a faster rate than the other ions (Fig. 15a). There are no major tributaries in this section of the river, so the increase in dissolved salts represented the combined effects of the groundwater inflow and returns from irrigation water. A significant saline inflow was recorded near Denman and, farther downstream, inflow of the Goulburn River resulted in a sustained increase in Na⁺, Cl⁻, and HCO₃⁻ and a temporary decrease in SO_4^{2-} concentrations (Fig. 15a). (The Hunter-Goulburn River junction also defines the boundary between the HFP1 and HFP2 hydrochemical provinces). Salinity of the Hunter River changed very little between the Goulburn River and Bayswater Creek confluences, showing that any groundwater inflow from the Permian rocks to the north was largely diluted by fresher groundwater from the Triassic escarpment to the south. A pronounced increase in total dissolved salts occurred between the Bayswater Creek confluence and Lemington; groundwater inflow in this section of the Hunter River was exclusively from the WI2 hydrochemical province, but its effect was diminished by the inflow of fresher surface water from Glennies Creek and Wollombi Brook. Apart from a minor increase in salinity below the Loders Creek confluence, the Hunter River water showed a progressive dilution in the large meanders around Singleton, most probably owing to interchange between the river and groundwater stored in the alluvium, perhaps induced by heavy well-pumping at that time. The low salinity of this water is surprising, since a large part of the meander belt is underlain by the Mulbring Siltstone, a unit associated with many saltaffected areas elsewhere in the upper Hunter River valley.

Salinity variation in base flow of the Wollombi Brook (Fig. 15b), a major southern tributary of the Hunter River, showed that rates of increase in Na⁺ and Cl⁻ were lowest in base-flow water in the section traversing the Triassic rocks and increased progressively through the Wollombi and Wittingham Coal Measures. The highest rates of uptake of Na⁺ and Cl⁻ coincided with a levelling-off in HCO₃⁻ concentration in the Wittingham Coal Measures just upstream from the Hunter River. Base-flow chemistry of Wollombi Brook therefore appears to be strongly controlled by lithology.

In Glennies Creek, a major stream draining a large catchment in the northeast of the study area, uptake of Na⁺, Cl⁻, and SO₄⁻ (Fig. 15c) increased considerably as the stream flowed across the Hunter Thrust Fault (which separates Carboniferous rocks in its headwaters from Permian rocks in its lower reaches). The Cl⁻ locus within 2 km of the fault zone was accurately located by intensive EC traversing. Significantly, the Cl⁻ concentration was found to increase several kilometres upstream from the Hunter Thrust Fault, indicating the extent of atmospheric recycling of Cl⁻ in the Glennies Creek valley. Conversely, significant increase in SO₄²⁻ was only detected in Glennies Creek downstream of the Hunter Thrust Fault.

The lower reaches of the Goulburn River showed very little variation in dissolved salts (Fig. 15d), apart from a sustained steep increase of Cl⁻ and Na⁺ and, to a lesser extent, Ca²⁺ and Mg²⁺ at its confluence with the Wybong Creek. Garman (1980) traced chemical variation in the Goulburn River from its headwaters in the Tertiary basalts to its junction with the Hunter River. He equated the progressive decline in HCO₃/Cl⁻ and (Ca²⁺ + Mg²⁺)/Na⁺ ratios in base-flow water with distance from silicate source in weathered basalt, and attributed the marked increase in Cl⁻ concentration in the lower reaches of the Goulburn River to inflow from the Wybong Creek.

The base-flow chemistry of the major tributary streams in the western part of the study area is shown in Figure 16. The headwaters of Wybong Creek to the north of the study area



Figure 15. Longitudinal variation in concentration of major ions. a — Hunter River, August 1982. b — Wollombi Brook, 5–6 August 1982.


Figure 15 (cont.). Longitudinal variation in concentration of major ions. c — Glennies Creek, 16 August 1982; d — Goulburn River, 3–4 August 1982.



Figure 16. Longitudinal variation in concentration of major ions. a — Wybong Creek, August 1982; b — Martindale Creek, 4 August 1982.



Figure 16 (cont.), Longitudinal variation in concentration of major ions. c - Sandy Creek, August 1982.

drain Tertiary basalt, where silicate weathering provides an abundant supply of HCO_3^- to base-flow water. However, in the section studied (Fig. 16a) the Wybong Creek only drains rocks of the Narrabeen Group. Steady increase in EC value was first detected about 0.5 km upsteam from the confluence with Big Flat Creek, but the highest salinity was measured at the junction of the two streams, where the introduction of highly saline bed underflow water from Big Flat Creek was greatest; however, this saline plume only became thoroughly mixed with Wybong Creek water about 2 km farther downstream.

Martindale Creek drains Wollombi Coal Measures for much of its course, but its tributaries drain Narrabeen Group rocks. The moderate rate of increase in base-flow salinity (Fig. 16b) in Martindale Creek is similar to that of the other north-flowing streams draining from the Triassic escarpment, but it was the only stream in which HCO_3^- was not the dominant anion. This probably reflects seepage from irrigation water because pumping of shallow groundwater from alluvial terraces is far greater in the Martindale Creek valley than in any other valley incised into the Triassic rocks to the east.

Base flow of Sandy Creek (Fig. 16c) is characterised by high Cl^- and HCO_3^- and low SO_4^{2-} concentrations in common with most other streams draining fractured rocks of the WI1 hydrochemical province (sample stations 81, 91 and 96 are bed-underflow samples, but lack confirmatory EC measurements between sampling points). Infiltration of Spring Creek water caused a substantial decrease in bed underflow salinity, though the dilution effect was negated a few kilometres downstream by the introduction of saline groundwater from the Wittingham Coal Measures. In August 1982,

surface flow in Sandy Creek commenced from seepages and outwash from bed-load gravels about 1 km upstream from station 235 (Fig. 16c). (It was not possible to obtain samples downstream from station 235, as holding ponds interrupt the natural flow regime.)

Of the two most prominent streams draining the Muswellbrook Anticline, Saddlers Creek, on the the western limb, showed marked increases in Na⁺ and Cl⁻ (Fig. 17a; Pl.2) and a concurrent decrease in SO₄²⁻ as it flowed from the Maitland Group rocks onto the Wittingham Coal Measures. Bayswater Creek drains the eastern limb of the Muswellbrook Anticline (Fig. 17b); the base-flow chemistry of its upper reaches in Maitland Group rocks is unknown, because its waters are impounded in the Elecom fly-ash dam and Lake Liddell. From Lake Liddell to station 105, base-flow characteristics of Bayswater Creek were obscured by artificial discharges and diversion associated with coal washery and mining activities. However, downstream from this point Bayswater Creek was relatively undisturbed, and under low-flow conditions its baseflow water probably approached equilibrium with groundwater of the Wittingham Coal Measures by the time it reached the Hunter River. The fundamental difference between base-flow chemistry in the lower reaches of Saddlers Creek and Bayswater Creek during August 1982 was that the former was characterised by WI1 hydrochemical province signature (low SO_4^{2-}/Cl^{-} ratio), whereas the latter exhibited the high SO_4^{2-}/Cl^{-} ratio typical of WI2 province groundwater.

Most streams in the northeastern part of the study area show changes in base-flow chemistry as they flow from Carboniferous rocks to the Permian sediments of the central lowlands.



Figure 17. Longitudinal variation in concentration of major ions. a — Saddlers Creek, 13–18 August 1982; b — Baywater Creek, 13–18 August 1982.

Unlike most other south-flowing streams in the CARB provinces, Bowmans Creek showed a small but steady decrease in dissolved salts as it approached the Hunter Thrust Fault (Fig. 18a). EC measurements between stations 163 and 132 decreased linearly and continuously throughout this section of the stream, indicating that the decline in base-flow salinity was caused by groundwater dilution rather than by tributary inflows. A marked increase in concentration of all ions occurred where Bowmans Creek traversed the Hunter Thrust Fault and intercepted groundwater from a small faulted block of Maitland Group sediments, an area whose land surface is dotted with severe salt scalds. Downstream from station 126, saline water discharging at a rate of about 30 L/sec from Foybrook Mine constituted the bulk of surface flow in Bowmans Creek and caused an abrupt change in the base-flow chemistry of the stream (high SO₄²⁻ and Cl⁻ concentrations at station 126 are characteristic of groundwater of the GM and lower WI2 (Vane Subgroup) provinces). Between Foybrook Mine (station 126) and the Swamp Creek confluence, baseflow salinity dropped sharply, mainly owing to dilution by alluvial groundwater, although a small part of the decrease in HCO_3^- and SO_4^{2-} concentrations was caused by the precipitation

of carbonate and sulphate minerals on the banks and low terraces of Bowmans Creek. Farther downstream, mixing and equilibration of Swamp Creek saline water with shallow groundwater of the alluvium resulted in a steady decrease in base-flow salinity in Bowmans Creek towards its junction with the Hunter River.

The rates of increase of the various ions in base flow of Swamp Creek (Fig. 18b) between stations 139 and 140 conformed with stream base-flow water in equilibrium with groundwater of the WI2 province, being characterised by approximately equal rates of enrichment of Cl^- , Na^+ and SO_4^{2-} , and constant or slowly declining HCO₃ concentration. Between stations 140 and 135, the channel of Swamp Creek has been diverted around the open-cut Swamp Creek Mine. Saline seepages from clay overburden dumps adjacent to the lower section of the diversion channel resulted in sharply increased concentrations of Cl⁻, Na⁺, SO₄⁻, and Mg²⁺ in base-flow water. Continually increasing EC value to a maximum of 12500 µS/cm (~7500 mg/L TDS) was recorded in base-flow water in the section through the non-vegetated overburden dumps. At station 135, immediately downstream from these dumps, the banks and bed-load sediments of Swamp Creek



Foybrook

Figure 18. Longitudinal variation in concentration of major ions. a — Bowmans Creek, 13, 14 August 1982.



Figure 18 (cont.). Longitudinal variation in concentration of major ions. b — Swamp Creek, 15 August. 1982.

were thickly coated halite, thenardite, and bloedite, which partly explains the sudden drop in SO_4^{2-} concentration (Fig. 18b). Downstream from here to its confluence with Bowmans Creek, Swamp Creek drains rural land; analyses from station 133 record a steadily decreasing base-flow salinity caused by groundwater mixing and dilution, even though the channel was coated with salt encrustations for most of this distance. Below station 133, the introduction of highly saline WI2 province groundwater resulted in a significant increase in Cl⁻ concentration.

In the headwaters of Muscle Creek (Fig. 18c) HCO₃ was the dominant anion in base flow traversing Carboniferous rocks above the Hunter Thrust Fault. Downstream through the Maitland Group rocks, rates of uptake of Cl⁻ and SO₄²⁻ rose, while HCO3 concentrations diminished slightly. Between stations 206 and 205, Muscle Creek crosses volcanics and marine sediments of the Dalwood Group; base-flow chemistry through the Dalwood Group rocks was characterised by increases in rates of enrichment of all ions except Cl-, which tapered off slightly. Below station 205, Muscle Creek re-enters Maitland Group rocks, but it was not practical to continue hydrochemical tracing, because of disturbance by urban development. Variations in ion concentrations in Muscle Creek base flow indicate that subtle differences are discernible in the groundwater chemistry of the pre-Wittingham Coal Measures Permian rocks, which suggests that some definition of the hydrochemical system is lost by combining these units together as a single province. A more satisfactory partitioning of the GM province would have separated the marine provinces (upper Maitland Group and lower Dalwood Group) from the intervening Greta Coal Measures, but partitioning of data would have resulted in a gross imbalance in group sizes and an excessive number of hybrids. The important difference, hydrochemically, between the Maitland and Dalwood Groups is that submarine volcanics are abundant in the latter, and groundwater of the Dalwood Group would therefore be expected to contain products of silicate mineral dissolution in addition to the background salts associated with a marine depositional environment.

Variations in concentrations of dissolved ions in Stringybark Creek are shown in Figure 18d; this stream was sampled in June 1983, ten months after the end of the drought. In addition to a base-flow component, the samples comprise an unknown proportion of interflow water, but, even in this flow regime, lithology clearly influences the stream-water chemistry — as shown by the rates of increase of Cl⁻, Na⁺, and SO₄²⁻ as the stream flows from Carboniferous to Permian rocks. Station 321 is a repeated sample of station 124 taken during the previous August; a comparison of ionic ratios distinctly shows the addition of dissolved CO₂ in the interflow water.

Previous examples have shown the common trend of increased Cl⁻ and SO₄²⁻ enrichment as streams cross the Hunter Thrust Fault from the Carboniferous rocks of the southern New England Fold Belt to the Hunter River floodplain entrenched in the Permian rocks of the valley floor. The base flow of streams within the CARB province therefore appears to be characterised by gradually increasing solute concentration, dominated by relatively uniform increments of HCO_3^- , and cations released by silicate weathering. However, in the eastern part of the CARB province base-flow composition seems to be more highly influenced by atmospheric recycling of salts within a 10–20 km radius of the boundary of the Permian source area.



Figure 18 (cont.). Longitudinal variation in concentration of major ions. c — Muscle Creek, 20 August 1982; d — Stringybark Creek, 20 August 1982.



Figure 18 (cont.). Longitudinal variation in concentration of major ions. e — Longitudinal variation in concentration of major ions and decline in HCO₃/Cl ratio, Goorangoola Creek, 16 August 1982.

The intensity of redistributed airborne salts in the eastern CARB province varies inversely with distance from the Hunter Thrust Fault, as shown by the variation in HCO_3/Cl^- ratio of base-flow water in the Goorangoola–Glennies Creek valley (Table 8).

TABLE 8. CHANGE IN MEAN HCO3:CL⁻ RATIO IN BASE FLOW OF GOORANGOOLA–GLENNIES CREEK VALLEY

Location	Trunk stream	Mean HCO3:Cl (concentration in meq/L)	Mean distance from Hunter Thrust Fault
Native Dog Creek)		0.8	13
Campbells Creek)	Goorangoola	0.65	8
Dawleys Creek)	Creek	0.5	2
Brandys-Sawyers) Creek)	Glennies Creek	0.4	2

Goorangoola Creek is entrenched into Carboniferous rocks in a meridional valley bounded by the Bullock and Razorback Ridges (Pl.2). The ascendancy of the solution of locally redistributed salts over silicate mineral dissolution as the dominant process controlling base-flow chemistry of Goorangoola Creek is clearly shown (Fig. 18e) by the downstream decline in HCO₃/Cl⁻ ratio. This trend was overprinted by mixing with water from Campbells Creek downstream from station 157; and by subsurface recharge through gravel aquifers of fresher water impounded by levees built around a former cut-off meander upstream from station 152 (see Pl.2).

The base-flow chemistry of two highly saline streams draining Permian rocks in the eastern and southeastern parts of the study area is shown in Figure 19. In Main Creek (Fig. 19a), base-flow salinity increased sharply about midway between stations 165 and 174, where the stream intersects massive conglomerate overlying the Bayswater coal seam. (2 kms further west this conglomerate coincides with what appeared to be a major source of salts in Bettys Creek.) Na⁺ and Cl⁻ concentrations declined rapidly in the Main Creek base flow downstream from the conglomerate, where its water mixed with shallow alluvial groundwater. It was not possible to decide whether the conglomerate stored considerable secondary salt that was diffusing into the stream or whether the impermeable nature of the conglomerate underbed induced stagnation of perched water with slowly increasing solute concentration by capillary zone losses.

Variations in base-flow salinity of Loder Creek (Fig. 19b) are a direct consequence of differences in structure and fracture permeability in the Permian rocks of the Wollombi Brook valley. The headwaters of Loder Creek drain coals and interseam sediments of the Jerrys Plain Subgroup, upper Wittingham Coal Measures (see Table 1), and large amounts of Na⁺ and Cl⁻ are taken into solution in its bed-underflow water. The Mount Thorley Monocline (Pl.1), which is defined by a local steepening of dip from angles of less than 10° to over 40°, appears to restrict lateral transmission of groundwater from the Wittingham Coal Measures through to the underlying Mulbring Siltstone of the Maitland Group; certain up-gradient salt springs in the Wittingham Coal Measures may well be generated by back-up and overspill of groundwater in response to this impediment. At depth this permeability restriction results in almost stagnant groundwater, and produces some of the most saline water in the upper Hunter River valley. A secondary consequence of this restricted groundwater throughflow is that groundwater spends a much longer time in the aquifers and thus equilibrates with a greater diversity of the less-soluble minerals in the coal seams. As Loder Creek

crossed the Mount Thorley Monocline, the salinity of the base flow showed a progressive decline, despite inflows from several highly saline tributaries draining the Mulbring Siltstone. However, from station 61 to its confluence with the Hunter River, the stream flows close to the axis of the Loder Dome and its base flow was diluted by fresher groundwater stored in sets of tensile fractures with enhanced permeability. There was also a noticeable increase in stream discharge along the Loder Dome.

The effect on the base-flow chemistry of upwelling groundwater from a structural discontinuity is shown in two streams in the northwest of the study area (Fig. 20). Spring Creek (Fig. 20a) and Big Flat Creek (Fig. 20b) intercept a vertical upward flow of saline groundwater, which has a strong WI2 province signature, along the trace of a diagonal fault transcurrent to the Mount Ogilvie Fault. Base-flow salinity in Spring Creek did not decline rapidly in response to groundwater dilution, because the decay loci were reinforced by an additional pulse of saline groundwater from the Denman Formation (top of the Wittingham Coal Measures — see Table 1) near station 86. The permeability of the Triassic rocks underlying the lower section of Big Flat Creek was not high enough to admit inflows of diluting groundwater sufficient to equilibrate the base flow with the TRIAS groundwater. In this respect, Big Flat Creek was the only stream measured in the study area where baseflow chemistry was completely dissimilar to the groundwater of the rocks through which it flowed.

In summary, the variations in base-flow chemistry of most rivers and tributaries in the study area indicate that the Permian rocks were the major source of salt loads in the upper Hunter River valley streams during August 1982; the addition of salts from saline groundwater and base flow traversing Permian hydrochemical provinces resulted in an increase in total soluble salts in the Hunter River from an initial concentration of 285



Figure 19. Longitudinal variation in concentration of major ions. a — Main Creek, 17 August 1982.



Figure 19 (cont.). Longitudinal variation in concentration of major ions. b — Loder Creek, 9–10 August 1982.

mg/L at Rouchel to 825 mg/L at Singleton. However, ephemeral concentrations of almost 1000 mg/L were recorded locally. Salinities would have been very much higher if diluting water had not been regularly released from the Glenbawn Dam, just north of the study area. Although base-flow measurements were taken under severe drought conditions, salt loads carried by streams in the first flush after rain would undoubtedly have been higher, owing to re-dissolution of efflorescent crusts in the stream channels. The variation in longitudinal concentration of the conservative ions in Figures 15 to 20 shows that there is considerable interaction between groundwater and base flow in the upper Hunter River valley streams, which testifies to the robustness of the system in dispersing saline pulses

generated both artifically and naturally. There has been considerable speculation about the effect of coal mining and related activities on water quality of the streams in the region. In this survey two instances of accelerated enrichment of solutes in base flow as a result of mining were detected in the Bowmans Creek catchment; however, without pre-mining base-flow measurements for comparison, it is not possible to assess objectively the quantity of solutes that could be attributed directly to mining, since groundwater in these areas is known to have high background salinity. The greatest uptake of salts by the streams was from natural sources: lithological differences and structural discontinuities in the Permian rocks.







Figure 20 (cont.). Longitudinal variation in concentration of major ions. b - Big Flat Creek, 29 August 1982.

CHEMICAL EQUILIBRIA

Data preparation

Not all sample analyses given in Appendix 1 are complete enough to use in equilibria interpretations, particularly with analyses of soluble SiO_2 and K^+ , although K^+ concentration was often estimated by the mean K^+ value of the particular hydrochemical province. As distribution of K^+ in the study area (Fig. 4) is nearly uniform, this procedure introduced only minor errors in the total chemical balance. Also, some samples were rejected on the basis of an unacceptable ionic balance, according to the constraint:

$$\frac{\Sigma[\text{cations}] - \Sigma[\text{anions}]}{\Sigma[\text{cations}] + \Sigma[\text{anions}]} > 0.10,$$

where ion concentration is in milli-equivalents per litre (meq/ $L). \label{eq:L}$

This screening yielded a data set of 491 samples distributed amongst the hydrochemical provinces as follows: CARB, 33; TRIAS, 17; WO, 87; HFP1, 31; HFP2, 77; WI1, 69; WI2, 100; and GM, 77.

Analytical concentrations were converted to molalities and the ionic strength (I) was obtained by the equation:

where m_i is the molal concentration, and z_i the valence of each ionic species.

Activity coefficients, Ψ_i , for each ionic species were obtained from the Debye-Huckel equation (Garrels & Christ, 1965):

$$\log \Psi_{i} = \frac{Az_{i}^{2}(I)^{\frac{1}{2}}}{1 + a_{i}B (I)^{\frac{1}{2}}}$$

where A and B are characteristics of H_2O , and a_i is the effective diameter of the ion in solution.

Various refinements of the Debye-Huckel equations are available (Stumm & Morgan, 1970), but as the ionic strength of the groundwater averages about 10^{-2} M, the errors involved in using the unmodified Debye-Huckel equation are negligible. Carbon dioxide pressure (P_{CO_2}), CO_3^{2-} and OH^- concentrations were then calculated by:

$$P_{CO_2} = (HCO_3^-). \Psi HCO_3^-.(H^+) \qquad \dots \dots (2),$$

$$(CO_{3}^{2-}) = \underbrace{K_{HCO_{3}} - K_{CO_{2}} \cdot P_{CO_{2}}}_{CO_{3}^{2-} \cdot (H^{+})^{2}} \qquad \dots \dots (3),$$

$$(OH^{-}) = K_{H_{3}O} \qquad \dots \dots (4),$$

$$OH^{-}(H^{+})$$

J.

where $K_{\rm CO_2}$ and $K_{\rm HCO_3^-}$ are the dissociation constants of the $\rm CO_2-H_2O$ system; $\rm K_{H_2O}$, the dissociation constant of $\rm H_2O$; and (HCO_3), the total dissolved CO_2. Brackets, (), are used to denote molal concentrations, and the activity of H^+ is taken as 1.0.

These values were then substituted back into equation (1) and the calculations reiterated to a constant ionic strength. At the same time, electroneutrality of the system was corrected by distributing the error amongst all the species in proportion to their contribution to the electroneutrality equation:

$$2(Ca^{2+}) + 2(Mg^{2+}) + (Na^{+}) + (K^{+}) + (H^{+}) = 2(CO_{3}^{2-}) + 2(SO_{4}^{2-}) + (HCO_{3}^{-}) + (CI^{-}) + (OH^{-}) \qquad \dots \dots (5).$$

All subsequent calculations were made from these 'filtered' data sets of molality and activity coefficients.

Disequilibrium indices

The potential for a mineral to crystallise from solution can be expressed in terms of a Disequilibrium Index: defined as the ratio of the ionic product of reactants to the thermodynamic solubility product of a given mineral (Paces, 1972). This can be explained most readily by the example of dolomite — $CaMg(CO_3)_2$: at equilibrium,

 $CaMg(CO_3)_2 = Ca^{2+} + Mg^{2+} + 2CO_3^{2-}$ and

$$\begin{split} K_{sp(dolomite)} \ &= \ [(Ca^{2+}). \ \Psi Ca^{2+}].[(Mg^{2+}). \ \Psi Mg^{2+}].[(CO_3^{2-}). \\ \Psi CO_3^{2-}]^2 \end{split}$$

where $K_{sp(dolomite)}$ is the solubility product of dolomite at 25°C and 1 atmosphere pressure. The Disequilibrium Index (Q) is then given by:

$$Q = \log_{10} \left| \frac{(Ca^{2+}) \cdot \Psi Ca^{2+} \cdot (Mg^{2+}) \cdot \Psi Mg^{2+} \cdot [(CO_{3}^{2-}) \cdot \Psi CO_{3}^{2-}]^{2}}{K_{sp(dolomite)} \cdot \dots \cdot (6)} \right|$$

where values for the numerator are obtained from the water analysis, and $K_{\text{sp}(\text{dolomite})}$ is obtained from published thermodynamic data.

When the analytical value equals the actual solubility product of the mineral in equation 6, Q equals zero and equilibrium is established. Positive values of Q indicate supersaturation, while negative values indicate undersaturation with respect to a particular mineral. Precipitation of authigenic minerals is theoretically only possible in supersaturated groundwater; conversely, mineral dissolution is a distinct possibility in undersaturated water. In mixed salt systems, values of Q ranging from -0.5 to +0.5 are generally taken to represent a state of equilibrium, because of the uncertainty in the analytical values and variation of K_{sp} in the presence of other ionic species.

A large number of minerals can be screened in this way, using computer programs such as WATEQ (Truesdell & Jones, 1974) or modifications. However, in this study only those minerals known or suspected to occur authigenically in significant quantities in the upper Hunter River valley have been compared with the water samples. (Congruent solubility products of minerals used for equilibria calculation are given in Table 9).

TABLE 9. CONGRUENT SOLUBILITY PRODUCTS (K°) OF MINERALS

			_
CaSO ₄ .2H ₂ O	Gypsum	2.399×10^{-5}	
CaCO ₃	Calcite	4.467×10^{-9}	
$CaMg_3(CO_3)_4$	Huntite	1.076×10^{-30}	
$CaMg(CO_3)_2$	Dolomite	1.0×10^{-17}	
Mg(OH) ₂	Brucite	7.079×10^{-12}	
MgCO ₃	Magnesite	1.0×10^{-8}	
$Mg_4(CO_3)_3(OH)_2$	Hydromagnesite	1.259×10^{-35}	
MgSi ₃ O ₆ (OH) ₂	Sepiolite	1.0×10^{-24}	
NaCl	Halite	3.819×10^{1}	
Na ₂ CO ₃ .10H ₂ O	Natron	4.89×10^{-2}	
Na ₂ SO ₄	Thenardite	6.62×10^{-1}	
$Na_2Mg(SO_4)_2.4H_2O$	Bloedite	4.169×10^{-3}	
NaAlCO ₃ (OH) ₂	Dawsonite	4.115×10^{-7}	
SiO ₂	Amorphous silica	1.995×10^{-3}	
Al(OH) ₃	Gibbsite	9.120×10^{7}	
Al ₂ Si ₂ O ₅ (OH) ₄	Kaolinite	4.677×10^{6}	
Na _{0 33} Al _{2 33} Si _{3 67} O ₁₀ (OH) ₂	Beidellite	1.122×10^{19}	
CaAl ₂ Si ₂ O ₈	Anorthite	5.012×10^{24}	
KAlSi ₃ O ₈	Microcline	2.188×10^{1}	
$Na_2Ca(SO_4)_2$	Glauberite	1.998×10^{0}	
SiO ₂	Chalcedony	2.999×10^{-4}	



Figure 21. Distribution of Disequilibrium Indices for the simple carbonate minerals calcite, magnesite and natron in upper Hunter River valley groundwater.



Figure 22. Distribution of calcite, magnesite and natron Disequilibrium Indices by hydrochemical province. 40

Simple carbonate minerals

Figure 21 shows the frequency distribution of Disequilibrium Indices for the total sample space, using calcite (CaCO₃), magnesite (MgCO₃), and natron (Na₂CO₃.10H₂O). Calcite and magnesite have very similar distributions, and their Q-values indicate that a large proportion of the water samples are in equilibrium or supersaturated with them; in some examples the calculated ion products were up to 100 times greater than that required for equilibrium. On the other hand, the Q value for natron averaged -8.0, thus indicating that simple sodium carbonates would not be expected in upper Hunter River valley aquifers.

A breakdown of the Q-values for calcite and magnesite (Fig. 22) showed that in all but the TRIAS and WO provinces, 81–97% of samples were saturated with respect to calcite; the percentage was only slightly lower for magnesite. Even so, approximately 50% of the WO samples and 30% of the TRIAS samples were similarly saturated. Disequilibrium Indices were not calculated for siderite (FeCO₃), since Fe was detected only in 8 of the 100 samples analysed for minor elements. It is therefore highly unlikely that precipitation of siderite can occur in the contemporary hydrogeochemical system.

Complex carbonate minerals

Complex carbonate species may be represented (Fig. 23) by minerals such as hydromagnesite — $Mg_4(CO_3)_3(OH)_2$, huntite — $CaMg_3(CO_3)_4$, dolomite — $CaMg(CO_3)_2$, and dawsonite — NaAlCO_3(OH)_2; the complex iron carbonate mineral ankerite, $Ca(Fe,Mg)(CO_3)_2$, was not compared to the water analyses because of the inhibiting Fe concentrations mentioned earlier. These complex carbonates show a high proportion of saturation and supersaturation, although the distribution of Q values is more widely dispersed than for calcite or magnesite. Hydromagnesite and huntite in particular show a polymodal distribution — Disequilibrium Indices range from +6 to < -12.5. Increasing the proportion of Mg^{2+} or OH^- in the mineral formula apparently reduces the possibility of equilibrium between complex carbonates and groundwater.

Partitioning the Disequilibrium Indices into hydrochemical provinces (Fig. 24) shows that the distribution of Q values for dolomite is very similar to that of calcite and magnesite. For hydromagnesite, W11, W12, and GM are the only provinces to show appreciable proportions of saturated samples, while huntite saturation is more widespread (38–68% of samples) over the HFP2, W11, W12, and GM provinces. Significantly, the solubility products (Ksp) of these complex carbonates are much lower than those for the simple carbonates; therefore, in theory, they should take priority in sequential precipitation from the Ca²⁺-Mg²⁺-CO₃²⁻ -OH⁻ system.

The remaining complex carbonate mineral dawsonite (Fig. 23) is comparatively abundant in the Permo-Triassic rocks of the upper Hunter River valley, despite its otherwise very limited global distribution. Disequilibrium Indices were calculated for only 93 samples, but are sufficient to show that the ionic products are well above the values of saturation with respect to dawsonite. The relatively high concentration of Na⁺ (10⁻² M) compared to approximately 10⁻⁵ M for both Al³⁺ and CO₃⁻² is partly responsible for the large Q values. The formation of dawsonite is unusual because it represents a combination reaction between alumino-silicate weathering, simple salt formation, and CO₂ pressure; presumably by the reaction of dissolved CO₂ with gibbsite:

$$Al(OH)_3 + HCO_3^- + Na^+ = NaAlCO_3(OH)_2 + H_2O.$$

High soluble-SiO₂ concentration would probably favour the formation of kaolinite from gibbsite (as discussed later), so dawsonite formation may be largely dependent on a highly specific leaching environment, involving removal of SiO₂ while allowing access of CO₂ and Na⁺.

All hydrochemical provinces are represented in the dawsonite distribution (Fig. 23), although only one sample from each of the CARB and TRIAS provinces is included. The GM and WI2 provinces contain the highest Q values, but since all samples were supersaturated with respect to dawsonite, little significance can be attached to this observation.



Figure 23. Distribution of Disequilibrium Indices for the complex carbonate minerals dawsonite, dolomite, huntite and hydromagnesite in upper Hunter River valley groundwater.



Figure 24. Distribution of dolomite, huntite and hydromagnesite Disequilibrium Indices by hydrochemical province.

Simple sodium minerals

Since sodium chloride is frequently associated with saline groundwater and salt efflorescence in the upper Hunter River valley, a comparison was made (Fig. 25) between halite (NaCl), mirabilite (Na₂SO₄.10H₂O), and natron (Na₂CO₃.10H₂O); (various other sodium sulphates and carbonates could have been used, but the minerals chosen represent the least-soluble forms). The large negative Q values (extreme undersaturation) indicate that none of these sodium salts could have formed within the contemporary groundwater system; concentrations in the order of 10⁶ to 10⁸ times the observed values would have been required to achieve saturation; however, the presence of halite and thenardite (the anhydrous form of mirabilite) in surface evaporite encrustations (Table 7) indicates the magnitude of the evaporative processes which concentrate these highly soluble salts.



Figure 25. Distribution of Disequilibrium Indices for the simple sodium minerals halite, mirabilite and natron in upper Hunter River valley groundwater.

Sulphate minerals

Gypsum (CaSO₄.2H₂O) was the most abundant and least undersaturated of the sulphate minerals (Fig. 26); mirabilite, bloedite, and glauberite showed increasing undersaturation over greater ranges of Disequilibrium Indices. Only about 5% of the samples, entirely within the WI2 and GM provinces, exhibited gypsum equilibrium; however, the high proportion of Q values between -0.5 and -1.5 in these provinces indicates that gypsum should be a significant product of early evaporative concentration. As gypsum is unlikely to form in high-bicarbonate water (because of the preference for Ca²⁺ to



Figure 26. Distribution of Disequilibrium Indices for the sulphate minerals gypsum, mirabilite, bloedite and glauberite in upper Hunter River valley groundwater.

combine with HCO_3^-), it would not usually form authigenic minerals in the alkaline groundwater of the upper Hunter River valley.

Bloedite ($(Na_2Mg(SO_4)_2.4H_2O)$ was identified in a number of evaporites (Table 7) and is considered to form by substitution of Mg^{2+} in the thenardite or mirabilite crystal structure. Glauberite ($Na_2Ca(SO_4)_2$) was not detected in this survey, despite its former abundance in the Mulbring Siltstone — as discussed previously. The very low Q values for glauberite indicate that it is extremely unlikely to form under present conditions, even as an evaporite, as it requires very low temperature to become a stable phase. Both bloedite and glauberite have similar multi-modal distributions (Fig. 27), which are well illustrated by glauberite for each hydrochemical province; the GM and WI2 provinces have considerably higher Q values, owing to their higher SO_4^{2-} status, but even so there is considerable variation within a number of the provinces.

The secondary (less undersaturated) mode in the mirabilite distribution (Fig. 26) is composed almost entirely of samples from the GM province, where 92% of samples had Disequilibrium Indices greater than -5.5.

Silica minerals

Amorphous silica (SiO₂) and sepiolite (MgSi₃O₆(OH)₂) were chosen to represent a large range of possible silicates; sepiolite was chosen because Mg²⁺ is the most likely cation to form a silicate in the presence of low aluminium concentrations. Although less-soluble minerals such as chrysotile (Mg₃ Si₂O₅(OH)₂.5H₂O) or talc (Mg₃Si₄O₁₀(OH)₂.10H₂O) would normally form in preference to sepiolite in this groundwater environment, they have not been identified in the upper Hunter River valley aquifers. Likewise, chalcedony is common in the study area, although amorphous SiO₂ is generally considered to be the most probable low-temperature silica form, despite its higher solubility.

Amorphous silica and chalcedony have very narrow ranges of Q values (Fig. 28). Chalcedony is displaced noticeably into the saturated zone (about 80% of the samples are saturated) and distribution in the individual provinces (Fig. 29) is remarkably consistent. For amorphous silica, relatively little increase in the SiO₂ concentration of groundwater would be required for equilibrium conditions. Hydrochemical provinces showing equilibrium with respect to amorphous silica are HFP2 (-0.5 < Q < +0.5 for 30% of samples), WI1 (20%), WO(20%), and







Figure 28. Distribution of Disequilibrium Indices for chalcedony, amorphous silica and sepiolite.

HFP1 (13%). In the contemporary leaching environment of the upper Hunter River valley, aqueous SiO₂ is derived from dissolution of silicate minerals, and hence the more aggressive the percolating groundwater, in terms of dissolved CO₂-induced acidity, the more SiO₂ would be expected in solution. A comparison of SiO₂ concentration and CO₂ pressure (Fig. 30) does not show a well-defined trend, although the components are significantly positively correlated (r = 0.37).

Sepiolite has a much smaller K_{sp} value than aqueous SiO₂, but does not exhibit a high degree of sample saturation. The OH moiety of sepiolite apparently results in a reduction and variation of Q value similar to the simple and complex carbonates. The WI1, WI2, WO, and HFP2 provinces have 12–13% saturated samples, whereas the TRIAS and HFP1 groups have none.

The role of carbon dioxide

The examples discussed above indicate that the carbonate systems are the most important systems in upper Hunter River valley groundwater. Sources of dissolved CO_2 include atmospheric CO_2 in recharge rainwater, oxidation of coal, and dissolution of carbonate minerals.

Computed CO₂ pressure (Fig. 31) averages around 10^{-2} atm compared with $10^{-3.5}$ for standard atmospheric pressure. Even allowing for possible losses of dissolved CO₂ during sample collection, this represents an active medium for silicate weathering — as discussed later.

The fact that ionic product often exceeds the solubility product of various carbonate minerals by several orders of magnitude indicates that other factors influence the initiation of precipitation reactions. In particular, the ionic strength of a solution can have a marked effect on the equilibrium constant of mineral systems (Block & Walters, 1968; Jurinak, 1984). Dolomite and calcite were observed in a number of surface salt encrustations, which accords well with the stability diagram for Ca and Mg carbonates at various CO₂ pressures (Garrels &



Figure 29. Distribution of chalcedony and sepiolite Disequilibrium Indices by hydrochemical province.



Figure 30. Relationship between soluble silica and the groundwater carbon dioxide partial pressure, upper Hunter River valley.



Figure 31. Distribution of carbon dioxide partial pressure in upper Hunter River valley groundwater.

Christ, 1965): magnesite and hydromagnesite are stable only at CO_2 pressures less than 10^{-6} atmospheres and Ca/Mg ratios of less than 10^{-3} — neither condition is commonly satisfied in upper Hunter River valley groundwater. When this groundwater is exposed to the atmosphere there is a loss of dissolved CO_2 , accompanied, less significantly, by a rise in pH, which can be calculated by rearranging the electroneutrality equation 5 as follows:

 $\begin{array}{l} 2(Ca^{2+}) + 2(Mg^{2+}) + (Na^+) + (K^+) - 2(SO_4^{2-}) - (Cl^-) = \\ 2(CO_3^{2-}) + (HCO_3^{-}) + (OH^-) + (H^+) & \dots \end{array}$

The right-hand side of the equation can be expressed in terms of (H^+) — as in equations (3) and (4) — together with

$$(\text{HCO}_{3}^{-}) = \frac{\text{K}_{\text{CO}_{2}} \text{P}_{\text{CO}_{2}}}{\text{HCO}_{3}^{-}.(\text{H}^{+})}$$

The left-hand side of equation 7 and activity coefficients for CO_3^{2-} , HCO_3^{-} , and OH^{-} are obtained as described previously and the equation is solved for H^+ . Iteration is used to achieve the final values at a prespecified level of accuracy.

Mean analytical values were taken for each hydrochemical province, and new pH values were calculated, assuming equilibration with atmospheric CO₂. Marked changes were observed (Fig.32): the pH of TRIAS and WO province samples increased by about 2.7 units, while samples from the remaining provinces averaged an increase of about 1.6 units. These changes, together with the new values of CO_3^{2-} , HCO_3^{-} , and OH^- , increase the Disequilibrium Indices, thus increasing the tendency to supersaturation and precipitation of pH-dependent minerals. This is clearly demonstrated for calcite (Fig. 33a, b) and sepiolite (Fig. 33c, d) in the WO and GM provinces, which were specifically selected on the basis of the clusters shown in Figure 32.



Figure 32. The effect on groundwater pH upon reaching equilibrium with atmospheric carbon dioxide.

A further consequence of carbonate precipitation from discharging groundwater is that Na⁺, Cl⁻, and SO₄²⁻ concentrations increase accordingly. Evaluation of the mixing effects with the atmosphere and surface water is not within the scope of the present study, but it is apparent that stream-water quality may be strongly dependent on the type of equilibrium reactions described above.



Aluminosilicates

Garrels & McKenzie (1967) proposed a weathering model (consistent with many groundwater compositions) in which minerals such as feldspars (high silica and cation contents) interact with CO₂-enriched water and leave a gibbsite residue; however, unless the dissolved silica is removed rapidly, kaolinite becomes the stable solid phase at the expense of gibbsite. Early stages of weathering are thus characterised by water composition consistent with kaolinite and very low soluble Al concentrations. As weathering of the primary minerals continues, silica and cation concentrations, and pH



19/156-1/45

Figure 33. a.b (left) — effect on calcite Disequilibrium Indices for a, WO and b, GM groundwater upon reaching equilibrium with atmospheric carbon dioxide. c,d (above) - effect of sepiolite Disequilibrium Indices for c, WO and d, GM groundwater upon reaching equilibrium with atmospheric carbon dioxide.

increase until montmorillonite forms. It is therefore likely that the composition of deeper groundwater, or that in prolonged contact with primary mineral grains, moves away from the gibbsite-kaolinite boundary towards kaolinite-montmorillonite equilibrium.

This proposed weathering model contrasts with the model of Jackson & Sherman (1953), but is supported by the results of Rai & Lindsay (1975); however, the two models are compatible under Garrels & McKenzies' (1967) assumption that the weathering products (silica and cations) accumulated in situ, whereas Rai & Lindsay (1975) assumed that the weathering products were rapidly removed by leaching. Undoubtedly, both situations occur in natural groundwater, where aquifer permeability, effective porosity, and position along flow lines have a large influence on the movement of weathering products, and hence either gibbsite or montmorillonite tend to become the stable mineral forms.

In applying thermodynamic principles to chemical weathering, a decision must be made as to whether congruent or incongruent dissolution will be considered. Rai & Lindsay (1975) considered congruent dissolution, in which a mineral dissociates into its individual components under the influence of H⁺; for example,

 $NaAlSi_{3}O_{8} + 4H^{+} + 4H_{2}O = Na^{+} + Al^{3+} + 3H_{4}SiO_{4}$ (low albite)

Garrels & McKenzie (1967) and Stumm & Morgan (1970), amongst others, reported such weathering in incongruent terms; such as

 $NaAlSi_{3}O_{8} + 4\frac{1}{2}H_{2}O + H^{+} = \frac{1}{2}Al_{2}Si_{2}O_{5}(OH)_{4} + 2H_{4}SiO_{4} + Na^{+}$ (low albite) (kaolinite)

Again, both approaches may be correct, depending on the hydrodynamic environment, but since rapid removal of weathering products is not likely and Al³⁺ concentrations are not unduly high (2 ppm), the incongruent relationship appears to be the more appropriate model for upper Hunter River valley groundwater; Figure 34 illustrates this weathering sequence, assuming calcic plagioclase anorthite (CaAl₂Si₂O₈) as the initial mineral. The solubility products used in this model are



Figure 34. Stability fields of some minerals in the Ca–Al–Si–H₂O system at 25° C as a function of Ca²⁺, H⁺ and soluble SiO₂. Points are from upper Hunter River valley groundwater and boundaries are from thermodynamic data of Stumm & Morgan (1970).

those of Stumm & Morgan (1970), who pointed out that the boundary conditions can vary markedly with the molecular formulae chosen for the solid constituents. This is particularly so for some of the plagioclase feldspars, in which isomorphous substitution within the crystal lattice is more common in the intermediate compositions than in the pure end-members.

Assuming the anticlockwise weathering sequence described previously, it can be seen that a number of upper Hunter River valley groundwater samples have very low soluble SiO_2 concentration, and hence are located in the gibbsite stability field, where their distribution within that field is an artefact of analytical detection limits. The only hydrochemical provinces not represented in the gibbsite stability field are HFP1 and HFP2; most samples are from the WI2 and GM provinces.

Only two samples appear to come under the control of anorthite, once again representing the WI2 and GM provinces.

Most samples lie within the kaolinite stability field and tend to congregate towards the kaolinite-montmorillonite boundary, as predicted for a model incorporating the accumulation of weathering products. In fact, 151 of the 493 samples are located within the montmorillonite field, which also includes 55% of the HFP2 samples. The TRIAS province has no montmorillonite representatives, while 15–30% of samples in the remaining provinces meet the equilibrium requirements. In general, this distribution conforms with the geomorphological environment: the TRIAS province occupies high ground, where rainfall infiltration is enhanced in the open colluvial soils, and soluble silica is likely to be removed fairly rapidly in



Figure 35. Relationship between the calcite Disequilibrium Index and the tendency for Ca-montmorillonite to form a stable phase in the upper Hunter River valley groundwater.



 $\log (SiO_2)$ Figure 36. Stability fields of some minerals in the Na–Al–Si–H₂O system at 25°C as a function of Na⁺, H⁺ and soluble SiO₂. Points are from upper Hunter River valley groundwater, and boundaries from a, thermodynamic data of Rai & Lindsay (1975) and b, Stumm & Morgan (1970).



Figure 37. Stability fields of some minerals in the K-Al-Si-H₂O system at 25°C as a function of K⁺, H⁺ and soluble SiO₂. Points are from upper Hunter River valley groundwater, and boundaries from a, thermodynamic data of Garrels & Christ (1965) and b, Rai & Lindsay (1975).

interflow and groundwater under the prevailing hydraulic gradients. Conversely, HFP2 groundwater represents a sink towards which weathering products from the surrounding uplands are directed.

It has been suggested (Stumm & Morgan, 1970) that calcite control of CO_2 pressure may exert considerable control on the weathering 'aggressiveness' of groundwater in high-Ca²⁺ environments. Since the carbonate system has been demonstrated to be a major feature of upper Hunter River valley groundwater, the tendency for calcite to form has been compared with the tendency for Ca-montmorillonite to be a stable phase, as shown in Figure 35, where the vertical axis represents the kaolinite–Ca–montmorillonite boundary derived from:

 $(\log K = \log (Ca^{2+}) + 8\log(H_4SiO_4) = -15.4)$ $(H^+)^2$

where () represents active concentration.

Calcite saturation occurs concurrently with a wide range of alumino-silicate stability conditions (Fig. 35), and in conjunction with gibbsite (Zone A), kaolinite (Zone B), and Camontmorillonite (Zone C); any causal interrelationship is therefore rather tenuous. This is not surprising, since silicate minerals are not the only source of Ca^{2+} in upper Hunter River valley groundwater. Marine transgressions, dissolution of carbonate minerals, and the continual influence of cyclic salt all represent past and present alternative sources of Ca^{2+} .

Figure 36 shows a similar type of analysis to that used in Figure 34, except that it traces the weathering of sodic plagioclase (albite) to Na-montmorillonite. It demonstrates the major difficulties associated with obtaining meaningful results with stability diagrams; that is, the need to ascertain detailed mineralogy of the aquifers and the solubility constants for these minerals. Two sets of mineral boundaries have been plotted in Figure 36, one from Stumm & Morgan (1970), the other from the free energy of formation (ΔG_f) data collated by Rai & Lindsay (1975). In the former, a large proportion of the water samples plot in the albite stability field, a few in the Namontmorillonite field, and the remainder largely in the kaolinite field. With Rai & Lindsay's data, virtually all the samples plot in the kaolinite field, and the montmorillonite boundary is displaced well into the zone where amorphous silica would be precipitated. Both sets of boundaries use the same mineral formulae, but there are obviously considerable differences in the incongruent dissolution solubility constants. Unless this information is known for specific localities, the results must be regarded only as an indication of the likely operative watermineral equilibria.

The equivalent plots for K-feldspar dissolution are shown in Figure 37 together with boundaries calculated from data provided by Garrels & Christ (1965) and Rai & Lindsay (1975). Again, there are considerable differences in the stability field boundaries, but in this case the general result is not affected greatly. Apart from those samples having very low soluble SiO₂, virtually all the remaining samples lie within the kaolinite stability field.

In summary, apart from the difficulties of boundary conditions described above, it would seem that most upper Hunter River valley groundwater has a composition compatible with kaolinite formation, placing it about mid-way through the chemical weathering cycle, regardless of whether accumulating or leaching conditions prevail. There is a tendency for the groundwater to plot towards the kaolinite–montmorillonite boundary, but, unfortunately, free energy of formation and solubility constants for montmorillonites of various compositions are poorly established, even for the pure end-members. However, the analytical approach demonstrated still remains valid, and the groundwater–aluminosilicate equilibria relationships in the upper Hunter River valley or any other groundwater system can only be refined after publication of further mineral solubility constants.

STATISTICAL ANALYSIS

VARIATION BETWEEN HYDROCHEMICAL PROVINCES

Canonical variates

Contrasts in the groundwater chemistry of eight hydrochemical provinces were analysed by the method of canonical variates (Rao, 1952).

Canonical variates analysis discriminates between (a priori) group means by generating linear functions of the variables for which the ratio of the between-groups mean square to the within-groups mean square is maximised subject to the within-groups mean square being set to unity. The eigenvalues (λ_i) are extracted from the characteristic determinant:

 $|BW^{-1} - \lambda I| = 0$

where

$$B = \frac{1}{k-1}H \text{ and } W = \frac{1}{n-k}E$$

- H = between-groups sums of squares and cross-products matrix;
- E = within-groups sums of squares and cross-products matrix;

I = identity matrix;

k = number of groups;

n = total sample size.

The dimensions of λ_i are reduced according to min(p, k-1), where p = number of variables.

The corresponding eigenvectors (\mathbf{c}_i) are derived from:

 $(BW^{-1} - \lambda I) (WC) = 0$

subject to the constraints: $C_i WC_i = 1$ for unit variance; and $C'_i WC_j = C'_i BC_j = 0$ so that the canonical vectors are uncorrelated for all i = j.

The first canonical vector, C_1 , is the direction of maximum variation between group means, C_2 is the direction of the maximum of the remaining variation, and so on for the third and subsequent vectors. The proportion of the total variance accounted for by the j largest canonical variates is given by the ratio:

$$\sum_{i=1}^{j} \lambda i / \sum_{i=1}^{\min(p, k-1)} \lambda i; j \leq \min(p, k-1)$$

The canonical variate scores of the ith group mean are given by:

 $Y_{i1} = C_1' (X_i - G), \dots, Y_{ir} = C_r' (X_i - G)$

where \mathbf{X}_i is the mean vector of the ith group,

and G is the vector of grand means.

Censoring and transformation of data

Only six variables were used in the canonical variates analysis, viz. HCO_3^- , Cl^- , SO_4^{2-} , Ca^{2+} , Mg^{2+} , and Na^+ . The K⁺ and SiO₂ were omitted because of the large number of missing values, and because of significant rounding errors

associated with detection limits of these ions in the laboratory. Measurements of pH were omitted because the true natural variation of this parameter was too sensitive to sampling errors. Electrical conductivity, or the regression estimate of total soluble salts, was omitted because it largely depends on the six major ions, and is therefore redundant.

The raw data were \log_{10} -transformed, partly to attempt to satisfy the necessary condition for canonical variates analysis of homogeneity of the covariance matrices of each group, but more importantly, to approach multinormality. If data are multinormally distributed, the canonical variates analysis transforms the within-groups' ellipsoids of variation to spheres in the space defined by the canonical axes. Therefore, a twodimensional graphical plot of the positions and inter-group distances of the canonical variate means may be greatly enhanced by delineation of confidence circles about the mean scores. It will be subsequently shown in the principal components analyses that the \log_{10} -transformation is indeed appropriate for the upper Hunter River valley groundwater data.

Results

The first four canonical roots and vectors are shown in Table 10.

TABLE 10. CANONICAL ROOTS AND VECTORS FOR UPPER HUNTER RIVER VALLEY HYDROCHEMICAL PROVINCES (log_{10} - transformed data; n = 670, p = 6, k = 8)

	Canonical vectors (loadings)				
Variable	1	2	3	4	
HCO ₃	0.31	0.98	4.28	1.07	
Cl-	-0.24	-2.34	0.52	3.90	
SO ²⁻	-0.87	0.91	0.06	1.38	
Ca ²⁺	-0.50	2.18	-1.15	-3.00	
Mg ²⁺	0.73	0.40	-0.51	-0.33	
Na ⁺	-1.89	-0.69	-1.38	-4.73	
Canonical root	1.60	0.77	0.19	0.07	
% variance	60.3	28.9	7.2	2.6	

As the canonical variate scores are adjusted for the grand mean, a positive/negative loading on a variable will generate a positive/negative contribution to a canonical variate score if the deviate of the group mean relative to the grand mean is positive. However, the magnitude of the contribution depends on both the deviate and the loading.

Interpretation of the canonical vectors (i)

The magnitude and signs of the loadings for the first canonical variate, Y₁, show that this vector primarily separates the groups according to Na^+ (strong negative) and SO_4^2 (intermediate negative) against Mg²⁺ (intermediate positive). Since SO_4^{2-} has the greatest between-group variance, its contribution to Y₁ scores is somewhat greater than the unstandardised loadings would indicate; similarly, the contribution of Mg²⁺ loadings on Y₁ scores is diminished because Mg²⁺ has the lowest variance of these three elements. In systems where a concept of growth is valid, the first canonical variate is generally a 'sizing' vector (Blackith & Reyment, 1971). In the present study, Y1 is not an absolute discriminator of size, because its loadings are of mixed signs; yet, ranking of group means along Y_1 is identical to a 'size' ranking by mean total (log-transformed) soluble salts. High positive scores are attained by groups where water is low in Na⁺ and SO₄²⁻; in the study area such water is generally of low salinity. Conversely, water high in Na⁺ and SO₄²⁻ produces high negative scores, and these two elements are always prominent in the highsalinity groundwater of the upper Hunter River valley area. Y₁ is therefore analogous to a sizing vector, because it orders

groups by salinity status, but the between-group separation along Y_1 is not proportional to arithmetic difference between mean total soluble salts of the provinces. Rather, separation is distorted according to the degree of relict marine influence indicated by Na⁺ and SO₄²⁻ (and Cl⁻) concentrations versus the relative influence of the contemporary continental leaching regime on the chemistry of the water; the continental signature is indicated by Mg²⁺ (and HCO₃) concentration, which is linked to silicate and carbonate mineral dissolution.

The second canonical variate, Y_2 , separates the provinces according to hydrochemical facies and is not connected in any way to salinity. Na⁺-Cl⁻-type water with negative scores is contrasted against Ca²⁺-SO₄²⁻ and Ca²⁺-HCO₃⁻-type water with a minor contribution from Mg²⁺ associated with the latter facies. Again, standardised SO₄²⁻ loadings make a greater contribution to Y₂ scores than does HCO₃⁻.



Figure 38. Canonical variate plot, showing salinity and facies variations of upper Hunter River valley groundwater. Based on six log₁₀-transformed variables. 95% confidence circles shown.

Figure 38 shows the separation of group means along the first and second canonical variates, which together account for 89% of the total sample variance. The $(+Y_1, +Y_2)$ quadrant contains the plots of the group means with the best quality groundwater of the upper Hunter River valley area; this water is characterised by low salinity — bicarbonate to chloride ratio greater than 1 and sodium adsorption ratio less than 3. Mean scores of the HFP1 and HFP2 provinces plot well within this field, while the CARB province plots marginal to the Y_1 axis, owing mainly to an increased proportion of Cl⁻ over HCO₃⁻ in areas proximal to the Hunter Thrust Fault.

The $(+Y_1, -Y_2)$ quadrant contains the means of the WO, WI1, and TRIAS provinces groups. The high positive Y_1 score for the TRIAS province is a consequence of its low salinity and the high negative Y_2 score is generated by low Ca^{2+} , SO_4^{2-} , and HCO₃⁻ concentrations relative to Cl⁻ and Na⁺. The WO group mean has a lower Y_1 score, primarily because of increased concentrations of Ca^{2+} and HCO₃⁻. The WI1 province plots close to the Y_2 axis because of its higher salinity, and its Y_2 score is not greatly different from that of the WO province group, since its increased Cl⁻ concentration is compensated for by concurrent increases in Ca^{2+} and HCO₃⁻

The GM and WI2 group means, which are widely separated from the other six provinces along Y_1 , have the highest



Figure 39. Canonical variate plot, showing facies and silicate dissolution variation of upper Hunter River valley groundwater. Based on six log₁₀-transformed variables. 95% confidence circles shown.

salinities, and therefore have high negative Y_1 scores. Furthermore, Y_1 divides the four Permian fractured-rock provinces into two clusters: the GM and WI2 group means are separated on the basis of their strong relict marine signature; whereas the WI1, WO provinces are clustered with the 'continental' groundwater provinces. The GM province is contrasted with the WI2 province along Y_2 , reflecting the sub-dominance of SO_4^{2-} in the anions of the GM province.

Loadings for the third and fourth canonical variates, Y_3 and Y_4 , have the unusual property of polarising anions (positive loadings) against cations (negative loadings). Together, Y_3 and Y_4 account for almost 10% of the total variation, and therefore order the groups in a non-random manner. Our interpretation of these vectors is that Y_3 separates groups according to the intensity of silicate and carbonate mineral dissolution, and Y_4 discriminates rates of mineral dissolution under a continental leaching regime against rates of molecular diffusion from the matrix of certain marine sedimentary rocks. Thus, Y_3 and Y_4 are process-response vectors. Separation of groups along Y_5 and Y_6 does not seem to be of any consequence.

A plot of group means relative to Y_2 and Y_3 is shown in Figure 39. Whilst these two variates account for only just over one-third of the total variation, they are nevertheless the most meaningful for understanding this system, since they indicate the relationship between hydrochemical processes and facies variations. In fact, Blackith & Reyment (1971) quoted many similar cases in morphometric applications of canonical variates analysis where physically important contrasts between groups have been attained, even with statistically insignificant vectors. In Figure 39, the distances between the TRIAS, WO and WI1, and WI2 group means mainly reflect their variation in Y_3 scores. The rays linking these provinces are schematic only, the unbroken lines represent direction of groundwater flow, and the broken lines indicate hydrochemical processes which are important in the genesis of the water. Groundwater originating by recharge in fractured rocks of the Triassic escarpment in the southern and western sections of the study area flows through the Wollombi Coal Measures on the lower hillslopes. The water which is not intercepted en route then flows through the Wittingham Coal Measures on the Hunter River valley floor and ultimately discharges into the floodplain alluvium. The mode of transmission varies from base flow in streams to interflow, shallow lateral throughflow, and deep circulation.

It has been shown that the topographic settings of the fractured-rock provinces dictate the hydraulic gradients; therefore, mean groundwater velocities are highest in the TRIAS province, next highest in the WO province, and lowest in the WI1 and WI2 provinces. Under conditions of rapid throughflow of recharge water initially low in H2CO3, hydrolysis of silicate minerals is retarded by the combined effects of low concentration of H⁺ ions and rapid groundwater velocities. Under slower flow regimes and continuing addition of vertical recharge water enriched in H₂CO₃, incongruent dissolution of silicates induces HCO3 concentration in proportion to the valency of the cations of the silicate minerals; the intensity of this process would be reflected in increasing Y₃ scores. Therefore, Y3 (Fig. 39) separates incipient silicate dissolution in the TRIAS province from incongruent silicate dissolution in the other provinces in which groundwater flow

rates are lower. The contrast depends highly on differences in groundwater velocity, and probably also on vegetation and soil characteristics. For carbonate minerals, the TRIAS–WO–WI1–WI2 groundwater flow path represents the progression from undersaturated to supersaturated conditions; that is, the high negative Y_3 score of the TRIAS province represents an active medium where carbonate minerals are being dissolved, whereas Y_3 scores closer to zero represent conditions where water is in equilibrium with respect to carbonates or areas where carbonates are being precipitated.

The separation of these groups along Y_2 reflects facies variations. In terms of processes, the broken rays in the direction of Y_2 (Fig. 39) probably represent dispersion of aerosols through the groundwater system; thus, these small distances can be regarded as Na⁺ and Cl⁻ background. In this context, aerosols are composed of locally redistributed salts in addition to a steady-state component of solutes in maritime rainfall.

The major proportion of groundwater leaving the upper Hunter River valley is of HFP2 composition, which at any instant in time can be considered as a mixture of the other seven groups. The large separation along Y_2 between the W11, W12 provinces and the HFP2 province (Fig. 39) is far greater than the distances representing dispersion of background salts from the TRIAS and WO provinces; it indicates molecular diffusion of dominantly Na⁺ and Cl⁻ from connate marine salts of the Wittingham Coal Measures. This input of Na⁺–Cl⁻-type water is strongly diluted by water of the HFP1 province (Fig. 39).

The contribution from the CARB province is approximately equally composed of the products of silicate and carbonate mineral dissolution (Y_3) and dispersion of background salts (Y_2) . The trend of local redistribution of salts to be maximised in the eastern part of the CARB province has been described, but it is also pertinent to note that the CARB province occupies the high country in the northeast of the study area (Pl. 2) and therefore probably receives higher rates of marine aerosols in rainfall. The GM province has a higher Y_2 score than the HFP2 province, primarily because of its higher SO_4^2/CI^- ratio. The magnitude of the Y_2 separation between these two provinces represents the algebraic sum of chloride (negative) and sulphate (positive) diffusion; the sense of direction indicates that sulphate diffusion dominates over chloride. The GM group also contributes products of carbonate mineral dissolution to HFP2 province groundwater from solution of carbonates in joints by acids released by sulphide oxidation, a mechanism which, incidently, explains the buffering of pH in this system.

Distances between groups

The complete linkage dendrogram based on log10-transformed data of the eight hydrochemical provinces is shown in Figure 40. The similarity measure is Mahalanobis's Generalized Distance. The provinces essentially form four clusters: TRIAS, CARB-HFP2-HFP1, WO-WI1, and GM-WI2.

Further partitioning of data

The eight hydrochemical provinces were divided into twenty-five subgroups (Table 11) and re-analysed by the method of canonical variates. The provinces were partitioned in such a way that the effects of geographic variation and differences in mode of transmission of groundwater could be assessed. An exception was the CARB province, where the split was done to test differences between the two major geological units alone, given that a division based on the wellestablished geographic variation in the CARB province would have contributed no new information. Again, the six variables were log₁₀-transformed.

TABLE 11. SUBDIVISION OF UPPER HUNTER RIVER VALLEY HYDROCHEMICAL PROVINCES FOR CANONICAL VARIATES ANALYSIS.

Subgroup	Parent	Description of subgroup	No. of samples
1)	Base flow, Wollombi Coal Measures	20
2)	Wells and bores; Bulga to Alcheringa	17
3) WO	Wells and bores; Broke valley north to Bulga	25
4)	Wells and bores, western Wollombi Coal Measures, Martindale valley to	31
)	northern boundary of study area	
5)	Surface samples, wells on lateral drainage from Carboniferous rocks, and	17
)	wells in direct hydraulic continuity with the Hunter River (100 m from bank)	
6) HFP1	Wells on lateral drainage from Wollombi Coal Measures.	21
7)	Wells on lateral drainage from Wittingham Coal Measures.	29
8)	Wells on lateral drainage from Maitland Group	19
9)	Surface samples, Hunter River	17
10)	Wells on lateral drainage from Maitland Group	44
) HFP2	Wells on lateral drainage from Wollombi and Wittingham Coal Measures	21
12)	Wells and bores, Lemington, on lateral drainage from Wittingham Coal Measures	23
13)	Base flow, lower Wittingham Coal Measures; Broke valley	26
14)	Base flow, lower Wittingham Coal Measures; Foybrook-Falbrook	39
15) w12	Bores in lower Wittingham Coal Measures	34
16)	Base flow, lower Wittingham Coal Measures; central area	19
17)	Base flow and wells, Branxton Formation and Greta Coal Measures	46
18) GM	Base flow and wells, Mulbring Siltstone	39
19)	Bores in Maitland Group and Greta Coal Measures	41
20)	Base flow, upper Wittingham Coal Measures	32
21) WI1	Wells, upper Wittingham Coal Measures	36
22)	Bores, upper Wittingham Coal Measures	22
23) TRIAS	Base flow, wells, and springs, Narrabeen Group	19
24		Base flow and wells, Gilmore Group	16
25) CARB	Base flow, Wallaringa Formation	17



Figure 40. Complete linkage dendrogram of upper Hunter River valley hydrochemical provinces, based on six log₁₀-transformed variables.

Results

The first four canonical roots and vectors are shown in Table 12.

TABLE 12. CANONICAL ROOTS AND VECTORS FOR UPPER HUNTER RIVER VALLEY HYDROCHEMICAL SUBGROUPS \log_{10} -transformed data, n = 670, p = 6, k = 25)

	Canonical vectors (loadings)					
Variable	1	2	3	4		
HCO ₃	0.24	0.61	-4.77	-1.08		
Cl-	0.82	-1.98	-0.33	-7.46		
SO2-	0.72	1.17	-0.01	-0.11		
Ca ²⁺	-0.15	2.66	0.58	-0.20		
Mg ²⁺	-0.77	0.06	1.03	2.61		
Na ⁺	1.76	-0.82	1.42	6.21		
Canonical root	1.96	1.29	0.53	0.18		
% variance	46.5	30.6	12.6	4.4		

Interpretation of the canonical vectors (ii)

The physical interpretation of separation between subgroups by these four new vectors is essentially the same as for the initial canonical variates analysis run on the eight groups. Likewise, Y₁ is a discriminator of size (TSS), except that signs of the loadings are reversed, and the weighting on Cl- is increased at the expense of SO₄²⁻; the latent discriminatory power of Y₁ in marine versus continental influence is preserved. Similarly, Y2 differentiates groups according to hydrochemical facies, except that positive scores are more highly identified with Ca²⁺-SO₄²⁻ than Ca²⁺-HCO₃⁻ water. Again, Y₃ and Y₄ (Table 12) are 'process' vectors, which contrast groups according to the intensity of silicate and carbonate mineral dissolution and diffusion of connate marine salts. However, in contrast to the initial canonical variates analysis, signs are reversed, loadings on Mg2+ are increased at the expense of Ca²⁺, and the components linked with diffusion and flushing of connate salts are almost exclusively identified with Cl⁻; the effect of SO_4^{2-} deviation on Y₃ and Y₄ scores is negated by low weights on SO_4^{2-} in both vectors.

Separation of the 25 subgroup means along the Y_1 and Y_2 vectors is shown in Figure 41. Subgroup means of the HFP1, HFP2, and CARB provinces plot in the $(-Y_1, + Y_2)$ quadrant, which is characterised by low TSS — Ca^{2+} is the dominant cation and SO_4^{2-} and/or HCO₃ the dominant anion(s). The Y_1 scores of the HFP1 subgroups (Fig. 41) show a gradual increase in salinity — from surface samples and wells receiving lateral drainage from Carboniferous rocks, to wells underlain by the Wollombi Coal Measures, to wells underlain by the Wittingham Coal Measures and Maitland Group. Y_2 , a strong



Figure 41. Canonical variate plot, showing salinity and facies variation of 25 subgroups of upper Hunter River valley ground-water. Based on six \log_{10} -transformed variables. 95% confidence circles shown.

positive discriminator of SO_4^{--} , separates those subgroups of the HFP1 and HFP2 provinces which comprise wells underlain by the Maitland Group rocks; this contrast implies significant groundwater mixing in certain areas of the floodplain alluvium, a feature that will be later explored by principal components analysis.

95% confidence circles of the CARB subgroups 24–25 (Fig. 41) intersect both clusters of HFP1 and HFP2 subgroups, showing that groundwater of the floodplain retains a strong Carboniferous province signature throughout the study area. The CARB–HFP2 link obtained in both sets of canonical variates analyses shows that a high proportion of wells of the HFP2 subgroups above Singleton are in direct hydraulic continuity with the Hunter River, because underlying lithological variations cause negligible difference in Y₁ scores for the means of the HFP2 subgroups distal to Maitland Group rocks.

In the $(-Y_1, -Y_2)$ quadrant (Fig. 41), which is characterised by water of low salinity (Na⁺ is the dominant cation and Cl⁻ the dominant anion), the 95% confidence circle of the TRIAS group (23) intersects confidence circles of the southern WO subgroups 2-3 of subsurface samples and the WO subgroup 1 of base-flow samples (which reflects the source of these streams in Triassic rocks). Y1 and Y2 separate the WO subgroup 4 from the TRIAS-southern WO cluster, principally because of significantly increased proportions of Ca^{2+} , SO_4^{2-} , and HCO₃ in WO subgroup 4. There are two explanations for this contrast: groundwater velocity is much lower in the western Wollombi Coal Measures and thereby permits a greater intensity of silicate dissolution, which completely overprints the TRIAS signature, or the increased Ca^{2+} and HCO_3^{-} concentrations are weathering products from either Tertiary basalts to the northwest or underlying dolerite intrusives. A concomitant substantial increase in mean Mg²⁺ concentration in WO subgroup 4 favours the hypothesis of silicate mineral dissolution from basic rocks.

The W11 subgroups are separated by Y_1 and Y_2 vectors into end-members — wells (subgroup 21) and bores (subgroup 22) — and intermediate base flow (subgroup 20). The distance between subgroup means indicates that, at the time of sampling, streams draining the W11 province were intercepting roughly equal proportions of shallowly and deeply circulating groundwater.

Means of the GM subgroups 17–19 have positive Y_1 scores, because of their high salinity, and positive Y_2 scores — (their anionic composition is such that SO_4^{2-} + HCO₃ > Cl⁻); these subgroups also have the highest Ca^{2+} concentrations. Subgroup 19 (bores in the GM group) is enriched in HCO₃, which, in this deeper water, may be due in part to oxidation of coal by sulphate. Subgroups 17 and 18 (base flow in the Mulbring Siltstone and Branxton Formation–Greta Coal Measures, respectively) have lower Y_2 scores because of increased mean Na⁺/Ca²⁺ and Cl⁻/(HCO₃ + SO₄²⁻) ratios; this reflects active flushing of diffused connate marine salts in the oxidation zone.

The WI2 subgroups 13-16 are high-salinity groundwater with Na⁺ the dominant cation and Cl⁻ the dominant anion. The increased concentration of all ions in subgroup 13, although with relatively minor changes in ionic proportions, separates this group from the other WI2 subgroups along Y_1 and Y_2 and suggests conditions of groundwater stagnation. The most likely concentration mechanism is a longer residence time in the aquifer, owing to impedance of groundwater throughflow by the Mount Thorley Monocline. The least saline base-flow water draining the Lower Wittingham Coal Measures was found in the northern part of the valley (subgroup 14). Y_1 and Y_2 scores for the central area (subgroup 16) are intermediate between subgroups 14 (north) and 13 (south) base-flow scores, and indicate that, for the WI2 subgroups, Y_1 increases and Y_2 decreases southwards, which reflects a sympathetic increase in Na⁺-Cl⁻ concentration gradient; in addition to structural controls related to the Hunter Thrust Fault, this may represent a

transition across a palaeogeographic boundary. During the Late Permian marine transgressions, the Wittingham Coal Measures closest to the Hunter Thrust would have had a great thickness of sediments saturated by the freshwater lens extending from the landmass of the New England Fold Belt.

Distance between subgroups

In the complete-linkage dendrogram of the 25 subgroups (Fig. 42), with Mahalanobis's D^2 as the similarity measure, clustering shows that the original relationships between the eight hydrochemical groups have been preserved with one exception — the TRIAS group is linked with the southern WO subgroups 2–3 and the W11 subgroups 20 and 22. This gives three main clusters: HFP1–HFP2–CARB, with some WO and W11 hybrids; WO–W11–TRIAS; and GM–W12.

Comparison of the canonical variates analyses

Results from the two canonical variates analyses are consistent. Angles between the two sets of canonical vectors are -27° (Y₁), 13° (Y₂), -10° (Y₃), and -33° (Y₄). Grouping in the first analysis was based solely on geological provenance, whereas the finer partitioning of data in the second analysis additionally incorporated geographic variation and, where possible, differences in mode of transmission (base flow, and shallow and deep groundwater). The fact that the integrity of the geological groups is maintained through both analyses testifies to the resilience of the data and shows that geological provenance is the single most important factor in influencing groundwater chemistry in the upper Hunter River valley.



Figure 42. Complete linkage dendrogram of 25 subgroups of upper Hunter Valley groundwater, based on six log₁₀-transformed variables.

VARIATION WITHIN HYDROCHEMICAL PROVINCES

Principal components

Principal components analysis (pca) is a long-established technique for investigating within-group dependence structures of multivariate observations. The p dimensions of correlated variables required for adequate description of the hydrochemical system are reduced by rigidly rotating the coordinate axes of the original observation space to the directions of maximum variation of the dispersion of sample points and generating q < p uncorrelated components as linear functions of the original variables.

The eigenvalues, λ_i , are extracted from the determinantal equation:

$$|S - \lambda I| = 0$$

where S = covariance matrix of observations, and I is the identity matrix.

The corresponding eigenvectors, \mathbf{a}_i , are derived from

S -
$$\lambda I$$
) $\mathbf{a}_i = \mathbf{0}$

subject to the constraints $\mathbf{a'}_i \mathbf{a}_j = 0$ for orthogonality, and $\mathbf{a'}_i \mathbf{a}_i = 1$ for uniqueness of the eigenvectors. The constraint for uniqueness also determines the property

$$Var(Y_i) = \lambda_i$$

where $Y_i = a_{1i}X_1 + \ldots + a_{pi}X_p$ is the ith principal component of the p-variate observation matrix X.

The first principal component Y_1 , associated with the dominant eigenvalue of S, explains the maximum proportion of the sample variance; the second principal component Y_2 , associated with the second largest eigenvalue of S accounts for the maximum of the remaining variance, and so on, for the third and subsequent principal components corresponding to successively smaller eigenvalues. The proportion of the total variance accounted for by the first j principal components is given by the ratio

$$\sum_{i=1}^{j} \lambda_i / tr(S); \ 1 \le j \le p$$

The principal component scores of the ith individual are $Y_{i1} = a'_{1}(X_{i} - G), \dots, Y_{ip} = a'_{p}(X_{i} - G)$

where X_i is the observation vector for the ith individual, and G is the vector of sample means.

In cases where the variables exhibit significant inequality of variance, the eigenvalues and eigenvectors are extracted from the sample correlation matrix R, and the principal component scores of the ith individual are then given by

$$\mathbf{Y}_{i1} = \mathbf{a'}_{1}\mathbf{z}_{i}, \ldots \mathbf{Y}_{ip} = \mathbf{a'}_{p}\mathbf{z}_{i}$$

where \mathbf{z}_i is the vector of standardised observations whose elements

$$\mathbf{z}_{ij} = \frac{\mathbf{x}_{ij} - \mathbf{g}_j}{\frac{\mathbf{s}_j}{\mathbf{s}_j}}$$

are the 'standard scores' of the original variables.

Methodology

As in the canonical variates analyses, only the six major ions, HCO_3^- , Cl^- , SO_4^{2-} , Ca^{2+} , Mg^{2+} , and Na^+ were used in the principal components analyses. Likewise, variables were log_{10} -transformed to stabilise variances, and two sets of principal components were extracted from each hydrochemical province — one from the S matrices and the other from the R matrices. Finally, the pooled data were subjected to two principal component analyses; eigenvalues and eigenvectors were extracted from the S and R matrices of log_{10} -transformed observations.

Results

The first three principal components from S and R matrices are shown in Table 13.

TABLE 13. PRINCIPAL COMPONENTS EXTRACTED FROM COVARIANCE AND CORRELATION MATRICES OF UPPER HUNTER RIVER VALLEY HYDROCHEMICAL PROVINCES (log₁₀-transformed data)

	Loa 1	udings (S 2	matrix) 3	Loa 1	dings (R 2	matrix
<u> </u>	,,		CARB p	rovince		
HCO ₃	-0.17	0.26	0.24	-0.44	-0.13	0.28
Cl-	-0.28	0.46	-0.48	-0.44	-0.04	-0.43
SO ₄	-0.86	-0.52	0.02	-0.23	0.95	0.19
Ca ²⁺	-0.21	0.35	0.52	-0.42	-0.18	0.48
Mg ²⁺	-0.27	0.49	0.32	-0.46	-0.19	0.20
Na ⁺	-0.20	0.30	-0.58	-0.41	0.05	-0.66
Eigenvalue	16.38	6.68	1.23	4.33	0.82	0.60
% variance	66.2	27.0	5.0	72.2	13.7	10.0
1100-	0.40	1	FRIAS p	rovince	0.24	0.40
HCO ₃	-0.49	0.02	-0.61	-0.42	-0.36	-0.49
CI⁻	-0.33	0.32	0.38	-0.46	0.26	0.27
SO ₄	0.44	0.84	-0.32	0.11	0.78	-0.61
Ca ²⁺	-0.46	0.10	-0.42	-0.43	-0.25	-0.46
Mg ²⁺	-0.43	0.33	0.34	-0.47	0.16	0.19
Na ⁺	-0.25	0.29	0.30	-0.45	0.33	0.24
Eigenvalue	22.50	12.92	2.81	4.08	1.31	0.42
% variance	57.2	32.9	1.2	68.0	21.8	/.0
			WO pro	ovince		
HCO ₃	-0.25	0.32	0.53	-0.37	0.43	0.59
Cl-	-0.40	0.29	-0.45	-0.46	0.05	-0.46
SO_4^-	-0.60	-0.79	0.02	-0.24	-0.89	0.16
Ca ²⁺	-0.36	0.19	0.53	-0.43	-0.06	0.44
Mg ²⁺	-0.41	0.27	0.03	-0.47	0.02	-0.04
Na ⁺	-0.35	0.27	-0.47	-0.44	0.13	-0.47
Eigenvalue	80.40	33.75	7.03	4.17	0.88	0.46
% variance	62.4	26.2	5.5	69.5	14.7	7.7
			HFP1 pr	ovince		
HCO_{3}^{-}	-0.12	0.11	0.01	-0.39	-0.22	0.24
Cl⁻	0.44	0.55	0.24	-0.48	-0.19	0.09
SO ₄	-0.76	0.61	-0.20	-0.34	0.45	-0.78
Ca ²⁺	-0.27	0.11	0.45	-0.43	0.32	0.10
Mg ²⁺	-0.23	0.12	0.49	-0.44	0.31	0.46
Na +	-0.28	0.54	-0.68	-0.35	-0.72	-0.34
Eigenvalue	28.21	11.11	4.43	3.43	0.95	0.63
% variance	60.2	23.7	9.5	57.2	15.8	10.5
1100-	0.10		HFP2 pr	ovince	a a a	0.00
HCO ₃	-0.18	0.18	-0.03	-0.45	0.02	0.09
CF	-0.25	0.41	-0.53	-0.45	-0.33	-0.24
SO ₄	-0.77	-0.63	-0.02	-0.16	0.88	-0.39
Ca ²⁺	-0.24	0.19	0.23	-0.42	0.24	0.52
Mg ²⁺	-0.45	0.56	0.54	-0.45	-0.04	0.39
Na +	-0.22	0.23	-0.62	-0.43	-0.23	-0.60
Eigenvalue	37.09	25.05	6.39	3.48	1.00	0.77
% variance	50.6	34.2	8.7	57.9	16.7	12.8
1100-	0.00	0.00	WII pro	vince	0.40	0.05
HCO3	-0.30	0.28	-0.29	-0.41	0.43	-0.05
CI ⁻	-0.47	0.24	-0.04	-0.49	0.09	-0.06
SO ₄	-0.52	-0.84	-0.11	-0.25	-0.59	-0.75
Ca ²⁺	-0.23	0.04	0.66	-0.34	-0.54	0.52
Mg ²⁺	-0.40	0.23	0.52	-0.45	-0.15	0.34
Na ⁺	-0.45	0.31	-0.45	-0.46	0.38	-0.22
Eigenvalue	88.72	38.05	14.51	3.76	0.98	0.76
% variance	58.9	25.3	9.6	62.6	16.3	12.7

	Loc	Loadings (S matrix)		Loadings (R matrix)		
	1	2	3	1	2	3
			WI2 pro	vince		
HCO ₃	-0.18	-0.17	-0.42	-0.38	0.51	0.45
Cl-	-0.44	-0.22	-0.22	-0.49	0.06	0.01
SO_4^-	-0.42	-0.52	0.58	-0.40	-0.09	-0.81
Ca ²⁺	-0.21	0.25	0.57	-0.27	-0.77	0.30
Mg ²⁺	-0.65	0.67	-0.12	-0.41	-0.25	0.23
Na ⁺	-0.37	0.38	-0.32	-0.48	0.27	-0.06
Eigenvalue	129.89	25.58	16.63	3.85	0.98	0.54
% variance	68.9	13.6	8.8	64.2	16.4	9.0
	GM province					
HCO ₃	-0.12	-0.43	0.54	-0.22	0.91	0.27
Cl-	-0.44	-0.41	-0.01	-0.46	0.01	-0.27
SO_4^-	-0.57	0.54	-0.34	-0.43	-0.27	-0.07
Ca ²⁺	-0.24	0.44	0.63	-0.34	-0.31	0.77
Mg ²⁺	-0.45	0.01	0.28	-0.49	-0.02	0.12
Na ⁺	-0.45	-0.42	-0.32	-0.45	0.05	-0.48
Eigenvalue	78.78	11.81	9.76	3.90	0.90	0.74
% variance	72.1	10.8	8.9	65.0	15.0	12.4
			Pool	ed		
HCO ₃	-0.19	0.27	-0.04	-0.37	0.43	0.56
Cl-	-0.43	0.38	0.23	-0.46	0.23	-0.21
SO_4^-	-0.65	-0.74	0.10	-0.37	-0.39	-0.59
Ca ²⁺	-0.24	0.01	-0.65	-0.37	-0.65	0.42
Mg ²⁺	-0.38	0.31	-0.53	-0.43	-0.14	0.19
Na ⁺	-0.41	0.36	0.48	-0.44	0.41	-0.29
Eigenvalue	1029.14	201.66	100.40	4.17	0.69	0.56
% variance	72.7	14.2	7.1	69.5	11.5	9.3

Interpretation of the principal components

Principal components from within-groups covariance matrices. In every case except the TRIAS group (Table 13) the coefficients of the first principal components from the S matrix, $Y_1(S)$, are all negative, and coefficients of the second and subsequent principal components ($Y_2(S)$,...) are of mixed signs. Both conditions are necessary and sufficient to conclude that $Y_1(S)$ is a sizing vector corresponding to concentration (TSS), which explains the variance in the HFP2 group ranging from 50% to 72% of the variance in the GM group; that is, the second and higher principal components are increasingly less important for explaining differences between individuals in groups with higher background salinity.

The second principal components, $Y_2(S)$, explain about a quarter of the variations in the CARB, WO, HFP1, HFP2, and WI1 groups with negative loadings on SO_4^{2-} and positive loadings for the remaining ions. $Y_2(S)$ therefore compares the species of highest variance (SO_4^{2-}) with other ions in the hydrochemical provinces having low to intermediate salinity, apart from in the TRIAS group, where $Y_1(S)$ and $Y_2(S)$ can be readily interchanged (Table 13) — an indication that, in this small sample space, the variation due to SO_4^{2-} is greater than the variation in total soluble salts.

In the two most saline hydrochemical provinces, WI2 and GM, the vector identified with size, $Y_1(S)$, accounts for about 70% of the total variance, whereas $Y_2(S)$ only explains 14% in the WI2 group and 11% in the GM group. In the WI2 group, $Y_2(S)$ is polarised between divalent ions with positive loadings and univalent ions with similar negative loadings; nevertheless, in both groups the second principal components are still strongly identifed with SO_4^2 , which, in both cases, is the most highly correlated variable with $Y_2(S)$, not only because its loadings are dominant or co-dominant, but also because SO_4^2 deviation from the mean is highest in these groups. It seems that, in higher salinity water, $Y_2(S)$ not only maintains the

TABLE 14. COMPARISON OF CHEMICAL FACIES FROM SIGNIFICANT Y₃(S) LOADINGS FOR UPPER HUNTER RIVER VALLEY HYDROCHEMICAL PROVINCES

Regional hydrological zone	Province	Chemical facies		
		Significant 'continental' loadings	Significant 'marine' loadings	
Boundary	CARB TRIAS WO	$\begin{array}{c} Ca^{2+}-Mg^{2+}-HCO_{3}^{-}\\ Ca^{2+}-HCO_{3}^{-}-SO_{4}^{2-}\\ Ca^{2+}-HCO_{3}^{-}\end{array}$	Na^+-Cl^- $Na^+-Mg^{2+}-Cl^-$ Na^+-Cl^-	
Intermediate	WI1 WI2 GM	$Ca^{2+}-Mg^{2+}$ $Ca^{2+}-SO_4^{2-}$ $Ca^{2+}-Mg^{2+}-HCO_3^{-}$	$Na^{+}-HCO_{3}^{-}$ $Na^{+}-HCO_{3}^{-}-Cl^{-}$ $Na^{+}-SO_{4}^{2-}$	
Mixing	HFP1 HFP2	$Ca^{2+}-Mg^{2+}-Cl^{-}$ $Ca^{2+}-Mg^{2+}$	Na ⁺ -SO ₄ ²⁻ Na ⁺ -Cl ⁻	



Figure 43. Sources of major ions in groundwater of the upper Hunter River valley.

discriminatory power of SO_4^{2-} , but also incorporates information on sulphate associations; a trend that may well be related to the propensity of SO_4^{2-} to form ion pairs and complexes in concentrated salt solutions.

As an exercise in data reduction, the first two principal components successfully explain 80-90% of the variance within each group; however, apart from demonstrating the importance of both salinity and SO_4^{2-} concentration, they do not elucidate hydrochemical processes in the study area. Y₃, although explaining only 5% of variation within the eight

hydrochemical provinces, is perhaps the most interesting of the $Y_i(S)$ vectors, as illustrated in Table 14 — the provinces are arranged in the order: boundary (regional recharge), intermediate (regional transmission-discharge), and mixing (regional sink) zones. The associated physical relationships between the various sources of ions and the dominant processes that affect their movement throughout the landscape are shown in Figure 43.

In the CARB and WO boundary provinces, $Y_3(S)$ compares Na⁺-Cl⁻ water with Ca²⁺-(Mg²⁺)-HCO₃ water and indicates a clear genetic distinction between 'marine' and 'continental' influences (parentheses indicate subordinate ion). Since these provinces have never been transgressed by marine water, the 'marine-related' constituents must represent combined dispersion of oceanic aerosols and locally redistributed Na⁺ and Cl⁻ in rainfall, although in the WO group a minor proportion of these salts is derived from upwards transmission of connate marine salts from the underlying marine units in the Wittingham Coal Measures. The 'continental-related' constituents reflect the key role of dissolved CO₂ in infiltrating rainfall and its interaction with soils and fractured rocks to release cations and soluble SiO₂ (not included as a variable in principal component analyses); the important processes are dissolution of alumino-silicate and carbonate minerals, oxidation of carbonaceous materials, and ion exchange.

In the TRIAS group, Y₃(S) contrasts 'marine' and 'continental' water signatures; there is an additional emphasis on mobility of the ions, and signs of the loadings are reversed. The convervative ions Na⁺ and Cl⁻ tend to move most rapidly through the system, whereas the divalent ions Ca²⁺, Mg² and SO₄²⁻ are more inclined to form ionic complexes and minerals which greatly reduce their rate of movement. Of the divalent ions, Ca2+ is most likely to be removed from groundwater by ion exchange, and SO_4^{2-} is susceptible to adsorption, particularly by silica and alumina gels, which are generally abundant in water in contact with oxidised coals. Thus, in the absence of vermiculite traps, Mg^{2+} is the most mobile divalent ion in the upper Hunter River valley groundwater. HCO₃ ions are intermediate in the sense that, although they are not involved in ion-exchange reactions, they are prominent in carbonate and silicate dissolution/precipitation reactions.

Hence, within the boundary hydrochemical provinces, $Y_3(S)$ primarily contrasts individuals according to the dominance of the Ca^{2+} -HCO₃ or Na⁺- Cl⁻ facies, while Mg²⁺ alternates between them, depending on the importance of the ionmobility factors. The processes operating within these hydrochemical provinces are solely governed by the reaction and transmission of dissolved CO2 and aerosols in infiltrated rainfall. Solute transport is dominated by convection and dispersion and there are no connate marine salts in the boundary provinces; however, the intermediate provinces, WI1, WI2, and GM, are more complicated systems because they have their own inherent characteristics, which tend to overprint the background partitioning of elements from rainfall infiltration; in certain areas they are modified by antecedent chemical signatures of groundwater transmitted laterally from adjacent provinces.

In the WI1 and WI2 groups (Table 14), HCO_3^- loadings in $Y_3(S)$ are no longer associated with the divalent cations, but are linked to Na⁺ loadings in the 'marine' facies water. The Na⁺- HCO_3^- association represents leaching and diffusion of connate marine salts, a process which is much slower than the convection and dispersion of elements in rainfall. To appreciate the significance of the Na⁺- HCO_3^- link, it is necessary to review the post-Permian chemical evolution of upper Hunter River valley groundwater. At the cessation of the final transgressive phase represented by the Denman Formation, interstitial water of the Wittingham Coal Measures and underlying sediments would have had a dominantly Na⁺-Cl⁻ composition. Even

though the near-surface palaeohydrologic regime during progradation of the overlying Wollombi Coal Measures and Triassic sediments was characterised by leaching under a continental freshwater environment, large-scale 'piston-flushing' of connate marine water from the underlying Permian sediments would have been possible only if the appropriate groundwater-seawater pressure differentials existed. At the time, it is quite likely that a large proportion of interstitial marine fluid in the deep sediments was expelled, as burial compaction caused a reduction in porosity; however, a considerable time lag probably occurred before matrix diffusion became a prominent factor in the chemical makeup of this water. Translocation of connate fluids from marine-influenced coal seams into adjacent coarse-grained sediments would have continued throughout the duration of rank advance of the coals. The major change in the hydrochemical regime of the upper Hunter River valley was maximisation of the groundwaterseawater potential difference as a result of Tertiary uplift and incision of drainage systems. Groundwater inflow from the Carboniferous and Triassic highland, and downwards percolation from the formerly extensive basalt caps would have been enriched in Ca^{2+} , Mg^{2+} , aqueous SiO₂, and HCO₃ from silicate mineral dissolution. In addition, igneous activity would have mobilised connate marine fluids in rocks of the WI1 province; cation exchange of Ca2+ for Na+ in the sodiumsaturated Permian sediments would have removed much of the available Ca²⁺ from solution in the infiltrating groundwater, leaving Na⁺ as the dominant cation. Initial groundwater outflow from the valley would have been dominantly Na⁺-Cl⁻ -rich because of the mobility of these ions, but, with continued flushing, Na⁺-HCO₃-type water would have become increasingly important in the effluent groundwater.

One way of representing the evolutionary path of groundwater from marine regression to equilibrium under a continental leaching hydrologic regime is by the sequence

$$Na^+-Cl^- \longrightarrow Na^+-HCO_3^- \longrightarrow Ca^{2+}-HCO_3^-$$

 $Y_3(S)$ scores indicate that pore water in the Wittingham Coal Measures has attained the second stage of this evolutionary sequence. Water in the WI1 group is more advanced in the sequence than that of the WI2 group, as shown by its association with relict Na⁺-Cl⁻-type water, which reflects the lengthy exposure of the WI1 province to flushing by meteoric water, as well as heating and mobilisation of connate marine water in a significant proportion of the WI1 province by the action of igneous intrusions.

Divalent ions in the 'continental' facies of the WI1 and WI2 provinces (Table 14) represent silicate and carbonate mineral dissolution or precipitation. The SO_4^{2-} association in the WI2 group is identified with the contemporary strong continental signature of oxidation of sulphides.

In the GM group, the process of diffusion of connate marine salts is most important, and it accounts for the maximum variation within this province, after elimination of the variation due to total soluble salts; that is, Y3(S) in the WI1 and WI2 groups is interchanged with Y₂(S) in the GM group, and the near-equal loadings for Cl⁻ and HCO₃ show that the GM groundwater is the least advanced of any group in the marineto-continental hydrochemical sequence. $Y_3(S)$ in the GM group represents a secondary dimension for comparing individuals according to 'marine' versus 'continental' influence: the 'marine' facies describes the Na⁺-SO₄²⁻ residue in the diffusion of connate marine salts after the variation in Clconcentrations along flow lines has been accounted for by $Y_2(S)$; the continental facies favours contemporary precipitation of carbonate minerals, (as in the WI1 province) with the dominant continental process of oxidation of sulphides having been described by $Y_2(S)$. The polarisation of ions in $Y_3(S)$ in the GM group (Table 14) is repeated in the fourth principal components in the other Permian fractured-rock provinces.

Finally, Y₃(S) loadings in the HFP1 and HFP2 groups cannot be readily separated into marine and continental facies, because the provinces cannot be considered as discrete systems in which only two genetically dissimilar hydrochemical processes are dominant. In fact, outputs from all processes which have been described by $Y_3(S)$ in the fractured-rock provinces (Table 14) can be expected to be inherited to varying degrees in the regional groundwater sinks of the floodplain. In general terms, $Y_3(S)$ is a 'mixing' vector which weighs the proportion of Carboniferous and Triassic water represented by the positively correlated loadings in the HFP1 and HFP2 groups against accession of saline groundwater from the Permian fractured rocks (represented by negatively correlated loadings). The ion associations indicate that the HFP1 province is sensitive to inflow of sulphate groundwater from the GM province, whereas in the HFP2 province input of chloride water from the Wittingham Coal Measures is more important; the locations of these inflows will be identified later by R-mode principal components. The interesting feature in the $Y_3(S)$ loadings for the floodplain provinces is the redundancy of the HCO_{3}^{-} variable in either system, which indicates that variations in HCO₃ concentrations throughout the floodplain are statistically of minor importance compared to the HCO₃ variations in groundwater of the fractured-rock aquifers.

Principal components from pooled covariance matrix. Table 15 shows the linear correlation coefficients of the principal components extracted from the pooled S matrix, $Yi(S_p)$, with log_{10} -transformed variables.

TABLE 15. CORRELATIONS OF PRINCIPAL COMPONENTS FROM POOLED COVARIANCE MATRIX OF UPPER HUNTER RIVER VALLEY HYDROCHEMICAL PROVINCES (log₁₀-transformed data).

	Principal component			
Variable	Yı	\dot{Y}_2	Y3	
HCO ₃	-0.64	0.41	-0.04	
Cl	-0.90	0.36	0.15	
SO ₄	-0.89	-0.45	0.05	
Ca ²⁺	-0.70	0.02	-0.60	
Mg ²⁺	-0.83	0.30	-0.37	
Na ⁺	-0.88	0.34	0.32	

Nearly 73% of the variance in upper Hunter River valley groundwater is explained by total soluble salts — as shown in Table 15 by the high negative correlations of $Y_1(S_p)$ with all \log_{10} -transformed variables.

In common with the within-groups results, $Y_2(S_p)$ compares negatively correlated SO_4^{2-} with the other variables, apart from Ca^{2+} , which is redundant because of its near-zero loading (see Table 13).

Similarly, $Y_3(S_p)$ contrasts individuals according to hydrochemical facies; the marine end-member is represented by Na⁺-Cl⁻ (positive loadings) and the continental end-members Ca²⁺ and Mg²⁺ (negative loadings). However, the important chemical evolutionary trend in groundwater of the Permian fractured rocks described by the within-groups pca does not figure in the pooled data. Environmental impact statements make extensive use of the sodium absorption ratio (SAR) to compare upper Hunter groundwaters. It is, therefore, of interest to note that ranking of individuals by $Y_3(Sp)$ scores is approximately the same as ranking them by SAR values, since

$$Y_{3}(Sp) = \log \left| \frac{Na^{0.48}}{Ca^{0.65} Mg^{0.53}} \right| + \log \left| \frac{Cl^{0.2} SO_{4}^{0.1}}{HCO_{3}^{0.04}} \right|$$

Neglecting the smaller term on the right-hand containing the anions

$$\begin{array}{l} Y_{3} \sim \frac{1}{2} \log \; \frac{(Na)}{CaMg} \; = \; \frac{1}{2} \; (\log \; Na \; - \; (\log \; Ca \; + \; \log \; Mg)) \\ \\ \text{but } \log \; (SAR) \; = \; \log \; \left| \frac{(Na)}{\frac{1}{2} \; (Ca \; + \; Mg)} \right| \\ \\ = \; \log \; Na \; - \; \frac{1}{2} \log \; (Ca \; + \; Mg) \; - \; \frac{1}{2} \log \frac{1}{2} \end{array}$$

 \sim ½ (2log Na - log (Ca + Mg)), omitting the additive constant.

Principal components from within-groups correlation matrices. In any system where a concept of 'growth' is valid, a principal components analysis will invariably generate a first principal component that is closely identified with 'size', especially for log-transformed data (Blackith & Reyment, 1971). In this study, the 'size' dimension is a measure both of groundwater salinity, which may be related to the abundance of total soluble minerals in a particular hydrochemical province, and the residence time of the groundwater in aquifers. However, Y_1 generally does not give much insight into chemical processes.

In a six-variable system, the second and third principal components must be relied on to carry out this task, and the most informative polarisation of vectors utilises cation-anion associations (hydrochemical facies) so that trends shown by samples along flow lines within and between facies may be linked to chemical processes. The comparison of individuals by facies should preferably begin with Y_2 , since it explains the maximum proportion of variance after total soluble salts. In a sense, the second principal components derived from the S matrices do not succeed in this regard, because the comparison of individuals is in terms of species (SO₄²⁻ versus the rest) rather than facies, an indication that the sample space is weighted too heavily by the unduly high variance of SO₄²⁻. To overcome this problem the variables were standardised by the transformation

$$_{ij} = \frac{\mathbf{x}_{ij} - \mathbf{g}_j}{\mathbf{s}_j}$$

7

which equates variances of each observation to unity. The principal components extracted from R, the covariance matrices of these standardised variables, are shown in Table 13.

The effect of changing from S to R matrices is to decrease the proportion of total variation explained by the first principal components by about 5% in the groups of highest ionic strength (WI2 and GM), and to increase it by a similar amount in each of the other groups. This trend is reversed in $Y_2(R)$; the average increase in the WI2 and GM groups is 4%, while the proportion in all other groups drops by an average of 12%. The amount of total variation explained by $Y_3(R)$ is increased by an average of 5% above $Y_3(S)$ uniformly across all groups.

The $Y_1(R)$ coefficients (Table 13) show that the first principal components from the within-group R matrices are all vectors of size, again with minor exception of the TRIAS group, which no longer shows an interchange of the Y_1 and Y_2 vectors, as was the case for components extracted from the S matrix. However, $Y_1(R)$ still orders individuals in the TRIAS province primarily on ionic strength, as shown by the almost equal loadings on HCO₃, Cl⁻, Ca²⁺, Mg²⁺ and Na⁺, which are four times the SO₄²⁻ weighting and of opposite sign.

In the CARB group, $Y_2(R)$ is positively correlated with SO_4^{2-} and negatively correlated with Ca^{2+} , Mg^{2+} , and HCO_3 ; Na^+ and Cl^- are redundant variables because of their near-zero loadings. In the TRIAS group, the comparison of individuals by $Y_2(R)$ is based on $Ca^{2+}-HCO_3^-$ (negative loadings) primarily against $Na^+-SO_4^{2-}$ and secondarily against $Na^+-Mg^{2+}-Cl^-$ (positive loadings). In the WO group, $Y_2(R)$ is essentially a speciation vector which compares negatively correlated SO_4^{2-} against positively correlated HCO_3^- . $Y_2(R)$ compares individuals of the floodplain provinces according to the facies relationships Na⁺-HCO₃-Cl⁻ with Ca²⁺-Mg²⁺-SO₄²⁻ (HFP1) and Na⁺-Cl⁻ with Ca²⁺-SO₄²⁻ (HFP2). In the WI1 group, Y₂(R) is negatively identified with Ca²⁺ and SO₄²⁻, whereas Na⁺ and HCO₃ have significant positive correlations.

The essential difference in Y_2 scores from the S to R matrices in the provinces of low to intermediate ionic strength is that the standardisation has, in most cases, introduced an ion association with SO_4^{2-} or, at the very least, has polarised the second principal components by species (i.e. the high variance of SO_4^{2-} is no longer the dominant factor in $Y_2(R)$, as it was in the S-matrix mode analyses).

However, in the higher salinity groups the usefulness of $Y_2(R)$ in elucidating hydrochemical processes is not greatly increased by the change from S to R mode. In the WI2 province, Na⁺-HCO₃⁻ water is compared with the divalent cations; ordering of individuals by $Y_2(R)$ in the WI2 province is somewhat similar to that of $Y_3(S)$, but with a 180° rotation. In the GM province, HCO₃⁻ is positively correlated with $Y_2(R)$, and Ca²⁺ and SO₄²⁻ are negatively correlated.

The polarisation of significant $Y_3(R)$ loadings is shown in Table 16. Note that $Y_3(R)$ explains an average of 10% of total within-group variances, twice that accounted for by the third principal components extracted from the covariance matrices.

TABLE 16. COMPARISON OF CHEMICAL FACIES FROM SIGNIFICANT $Y_3(R)$ LOADINGS FOR UPPER HUNTER RIVER VALLEY HYDROCHEMICAL PROVINCES

Regional Province hydrological zone		Chemical facies		
		Significant 'continental' loadings	Significant 'marine' loadings	
Boundary	CARB TRIAS WO	$Ca^{2+}-Mg^{2+}-HCO_{3}^{-}-SO_{4}^{2-}$ $Ca^{2+}-HCO_{3}^{-}-SO_{4}^{2-}$ $Ca^{2+}-HCO_{3}^{-}-SO_{4}^{2-}$	Na^+-Cl^- $Na^+-Mg^{2+}-Cl^-$ Na^+-Cl^-	
Intermediate	WI1 WI2 GM	$Ca^{2+}-Mg^{2+}$ $Ca^{2+}-Mg^{2+}-HCO_{3}^{-}$ $Ca^{2+}-HCO_{3}^{-}$	Na ⁺ -SO ₄ ²⁻ SO ₄ ²⁻ Na ⁺ -Cl ⁻	
Mixing	HFP1 HFP2	$Mg^{2+}-HCO_{3}^{-}$ $Ca^{2+}-Mg^{2+}$	Na ⁺ -SO ₄ ²⁻ Na ⁺ -SO ₄ ²⁻ -Cl ⁻	

In the CARB, TRIAS, and WO boundary provinces, $Y_2(R)$ contrasts individuals on the basis of 'marine' (Na⁺-Cl⁻) versus 'continental' (Ca²⁺-HCO₃⁻SO₄²⁻ influences; again, the linkage with Mg²⁺ depends upon whether ion mobility is important within the system. The only difference between $Y_3(R)$ and $Y_3(S)$ scores is that SO₄²⁻ makes a much larger contribution to the 'continental' component of the $Y_3(R)$ scores. A similar interpretation of the physical meaning of the R-mode facies is involved here, namely that the Na⁺-Cl⁻ type represents the process of rapid convection and dispersion of conservative ions in aerosols, and the Ca²⁺-HCO₃⁻ facies reflects slower silicate and carbonate mineral dissolution. The incorporation of SO₄²⁻ into the latter facies represents dissemination of this ion from the continental sulphate store.

In the WI1, WI2, and GM groups the marine-to-continental evolutionary trend of flushing of interstitial marine fluids, ionexchange, and diffusion of connate marine salts, previously described by $Y_3(S)$, is now explained by $Y_2(R)$, which also discriminates sulphide oxidation as the most important continental-type process in these rocks. $Y_3(R)$ contrasts individuals on the basis that the carbonate dissolution/precipitation reaction represents the 'continental' process responsible for the largest independent variation in the system after that resulting from sulphide oxidation is taken out, and the 'marine' Na⁺-SO₄²⁻-Cl⁻ association describes the role of sulphate as a residual in diffusion of connate marine salts. The low weighting of SO₄²⁻ in Y₃(R) for the GM province implies that sulphate concentration gradients due to molecular diffusion are insignificant when compared to variations in SO₄²⁻ concentration generated around zones of sulphide oxidation.

The third principal components in the floodplain groups are 'mixing' vectors, whose interpretation is now much more straightforward in the light of the above $Y_3(R)$ results for the boundary and intermediate provinces. In the HFP1 and HFP2 provinces, the $Ca^{2+}-Mg^{2+}-(HCO_{3})$ association is inherited from the 'continental' processes of silicate and carbonate mineral dissolution, predominantly from the CARB province. The contrasting $Na^+ - SO_4^{2-} - (Cl^-)$ 'marine' association is identified with the component of saline groundwater inflow from adjacent Permian rocks and is attributable to diffusion of connate marine salts. The molecular diffusion process is assumed to be independent of the much more rapid process of sulphide oxidation, whose effects were described by $Y_2(R)$. In terms of relative mobilities of chloride and sulphate ions in solution, early stage diffused groundwater would be enriched in Cl⁻ and later stage water would exhibit SO_4^{2-}/Cl^{-} ratios somewhat in excess of the base-line oceanic level of 0.1 (in meq/L). Hence the Na^+ -SO₄²⁻ facies groundwater from the Permian rocks contiguous with the HFP1 province represents later stage water than the Na^+ - SO_4^{2-} - Cl^- association in rocks draining into the HFP2 province. Therefore, Y₃(R) implies that the rocks adjacent to the HFP1 province are more highly leached than those further down the valley, peripheral to the HFP2 province. The difference in the contribution of $HCO_{\overline{3}}$ loading between the two HFP groups indicates that the influence of the Carboniferous source area diminishes with increasing distance downstream. This trend in no way contradicts the close similarity observed between the HFP2 and CARB group means by canonical variates analysis, because $Y_3(R)$ is an independent measure of the third most important factor after the dominating effects of size (TSS) and 'rapid' thermodynamics have been separated out.

Principal components from pooled correlation matrix. Correlation relations between \log_{10} -transformed variables and the first three principal components extracted from the pooled correlation matrix are shown in Table 17.

TABLE 17. CORRELATIONS OF PRINCIPAL COMPONENT SCORES FROM POOLED CORRELATION MATRIX OF UPPER HUNTER RIVER VALLEY HYDROCHEMICAL PROVINCES (log₁₀-transformed data).

	Principal Component				
Variable	Υ,	Ý ₂	<i>Y</i> ₃		
HCO ₃	-0.76	0.36	0.42		
Cl-	-0.93	0.19	-0.16		
SO ₄ ²⁻	-0.76	-0.32	-0.44		
Ca ²⁺	-0.75	-0.54	0.32		
Mg ²⁺	-0.88	-0.12	0.14		
Na ⁺	-0.90	0.34	-0.21		

The dimension identified with total soluble salts, $Y_1(R_p)$, takes up almost 70% of the total variance. $Y_2(R_p)$ and $Y_3(R_p)$, which explain 12% and 9% of the variation respectively, are independent measures of the strength of relict 'marine' versus 'continental' hydrogeologic influences on the groundwater composition of individuals; that is, $Y_2(R_p)$ and $Y_3(R_p)$ scores show how far removed individuals are from equilibrium with a fresh-water leaching environment.
In $Y_2(R_p)$, the negatively correlated ion association $Ca^{2+}-Mg^{2+}-SO_4^2$ dominantly represents sulphide oxidation in highsalinity water, while in low-salinity water it is identified with silicate and carbonate mineral dissolution. The contrasting $Na^+-HCO_3^--Cl^-$ facies is linked with matrix diffusion of intermediate-stage marine interstitial fluids and connate salts in high-salinity groundwater, and dispersion of aerosols in lowsalinity water.

In $Y_3(R_p)$, the comparison is $Ca^{2+}-Mg^{2+}-HCO_3^-$ (the signature of silicate and carbonate mineral dissolutionprecipitation reactions and the role of dissolved CO_2 in infiltrated meteoric water) against the $Na^+-SO_4^2-Cl^-$ facies, which again is identified with diffusion of later stage connate marine water and salts. The essential difference between the representations of marine-facies water in the second and third principal components is that $Y_2(R_p)$ depends on the interaction of meteoric and connate water and includes cation exchange; $Y_3(R_p)$ is an independent measure of the sulphate residual in connate water induced by the difference in mobility between chloride and sulphate ions in solution.

Consistency of principal components analyses

Table 18 shows that corresponding angles between the three sets of vectors are significantly different, with the largest variations occurring in the second and third principal components. This is almost entirely due to the high SO_4^{2-} variance.

TABLE 18. ANGLES BETWEEN CORRESPONDING SETS OF PRINCIPAL COMPONENTS DERIVED FROM S AND R MATRICES OF SIX LOG₁₀- TRANSFORMED VARIABLES, UPPER HUNTER RIVER VALLEY GROUNDWATER

$Y_1(S) \wedge Y_1(R)$	$Y_2(R) \Lambda Y_{\ell}R)$	$Y_3(S) \Lambda Y_3(R)$
46°	-46°	13°
24°	32°	21°
23°	28°	11°
33°	-44°	48°
44°	-46°	34°
18°	45°	44°
19°	-59°	-60°
11°	-46°	32°
21°	54°	-50°
27°	44°	35°
	$\begin{array}{c} Y_{I}(S) \ \Lambda \ Y_{I}(R) \\ 46^{\circ} \\ 24^{\circ} \\ 23^{\circ} \\ 33^{\circ} \\ 44^{\circ} \\ 18^{\circ} \\ 19^{\circ} \\ 11^{\circ} \\ 21^{\circ} \end{array}$	$\begin{array}{c c} Y_{1}(S) \ \Lambda \ Y_{1}(R) \ Y_{2}(R) \ \Lambda \ Y_{1}(R) \\ \hline 46^{\circ} & -46^{\circ} \\ 24^{\circ} & 32^{\circ} \\ 23^{\circ} & 28^{\circ} \\ 33^{\circ} & -44^{\circ} \\ 44^{\circ} & -46^{\circ} \\ 18^{\circ} & 45^{\circ} \\ 19^{\circ} & -59^{\circ} \\ 11^{\circ} & -46^{\circ} \\ 21^{\circ} & 54^{\circ} \\ \hline 27^{\circ} & 44^{\circ} \end{array}$

In the S-mode first principal components, SO_4^{2-} has either the dominant loading or is co-dominant with Cl⁻. When deviations from the mean are included in $Y_1(S_p)$ scores, it is evident that SO_4^{2-} is the most important single contributor to the ordering of individuals by size (TSS). However, when variables are standardised, the relative contribution of SO_4^{2-} is no greater than the other variables in the $Y_1(R)$ and $Y_1(R_p)$ scores.

The dominance of SO_4^{2-} carries through to the second principal component in all the S-mode analyses, and, since $Y_2(S)$ and $Y_2(S_p)$ are essentially speciation vectors, there is no clear distinction between the various sulphate-producing processes. The S-mode second principal components seem rather to have a closer association with the activity of sulphate in solution. Conversely, $Y_2(R)$ and $Y_2(R_p)$ also have prominent SO_4^{2-} loadings, but these vectors additionally include ion associations which may be related to hydrochemical processes. In this case, the dominant influence of SO_4^{2-} loading in R-mode second principal components of the Permian fractured-rock provinces is a consequence of sulphide oxidation.

The comparison of individuals by their S and R-mode Y_3 scores is similar, in the sense that they are discriminated primarily by the relative influence of relict 'marine' versus 'continental' influences. However, since so much of the SO₄²⁻

variance has been taken up in the first two S-mode components, it does not often figure prominently in the third vector. In contrast, $Y_3(R)$ and $Y_3(R_p)$ are not constrained in this manner, so substantial SO_4^{2-} loadings are present in most of the R-mode third principal components. This accounts for the dissimilarity in $Y_3(S)$ and $Y_3(R)$. Again, hydrochemical processes independent of those derived from Y_2 may be inferred from ion associations in $Y_3(R)$ and $Y_3(R_p)$.

In all future discussion of principal components, the $Y_i(R_p)$ form will be used. The R-mode analysis is preferred, since cause-and-effect relationships are more readily identified from the second and third components. The pooled correlation matrix is used because of the difficulties in translating from one within-group observation space to another, and also for the philosophical reason that the only discrete hydrochemical provinces in the study area are the TRIAS and CARB groups; in all others the proportion of groundwater which is not derived from within-group infiltration will bear an antecedent signature of the upgradient province. However, even the CARB and TRIAS groups cannot be considered as truly independent, since cyclic salts deflated from the lower lying provinces are redeposited in their border areas.

Clustering by principal components

Plots of Y_1 and Y_2 scores from the pooled correlation matrix are shown in Figure 44. For clarity of presentation, the plots have been divided into hydrochemical provinces (Fig. 44a–g); however, when all points are superimposed onto the one plot, an approximate elliptical scatter of data is attained — a favourable indication that the log_{10} -transformed variables are close to being multinormally distributed (Blackith & Reyment, 1971).

Figure 44a-g depicts groups of individuals from hydrogeological catchments. Separation of clusters permits visual assessment of the similarity between groundwater catchments within the same hydrochemical province, and, as such, does not warrant a detailed description here. Aspects which should be borne in mind are that the spread of within-catchment Y1 scores primarily reflects residence time, and variations along Y₂ show the relative strength of modern 'continental' processes with negative scores versus relict and contemporary 'marine' influences with positive scores. For example, Y2 scores of base flow and subsurface samples from Wollombi Brook, Martindale Creek, Doyles Creek, and Milbrodale Brook catchments in the WO group (Fig. 44b) show a dominant 'marine' influence, but the positive Y1 scores indicate that the catchments are of low salinity - a combination which, together with the geomorphic settings of these valleys, has previously been closely identified with the relatively rapid process of dispersion of aerosols in rainfall. These four streams have a substantial TRIAS input, as shown by their proximity to the TRIAS mean (Y1, Y2) score, and they are, in fact, the streams of greatest length in the south of the area. The other streams draining the southern escarpment are much shorter, and their catchments have smaller reliefs; they form the cluster of Hayes Creek, Appletree Creek, and Wambo Creek (Fig. 44b), which is almost equally influenced by 'marine' (rapid transmission of univalent ions) and 'continental' (slower dissolution/precipitation reactions of divalent ions) processes, a consequence of lower hydraulic gradients dictated by subdued relief. These two major clusters may in turn be compared with catchments incised into the western escarpment, namely Spring Creek, Big Flat Creek, and Sandy Creek-Coal Creek (Fig. 44b); this cluster is dominated by slow, 'continental' processes, mainly silicate mineral dissolution. In this regard, it is interesting to note the similarity of scores of Spring Creek water with the corresponding scores of bore and well water from the Fordwich Sill, a major dolerite intrusion in the Wollombi valley. An association between mineral dissolution



Figure 44. Clustering by principal component scores of salinity and facies variation for 670 individuals of upper Hunter River valley groundwater. Based on six \log_{10} -transformed variables. Principal components from pooled correlation matrix. a — CARB-TRIAS, b — WO, c — HFP1, d — HFP2, e — WI1, f — WI2, g — GM; h — Hydrochemical processes represented by principal component scores. Mean scores of hydrochemical provinces shown.



in basic rocks and groundwater of the western Wollombi Coal Measures was inferred in the canonical variates analysis; pca has independently identified a more specific link with the Spring Creek valley.

In summary, the plots of principal component scores (Fig. 44a-g) basically partition data into four fields, each one associated with a particular hydrochemical process and a central mixing zone (Fig. 44h). Points in the $(+Y_1, +Y_2)$ quadrant distant from the origin are primarily identified with the steady-state dispersion of aerosols. Compared with other hydrochemical processes in the upper Hunter River valley, dispersion of aerosols is rapid and is important in the TRIAS and WO provinces. The $(+Y_1, -Y_2)$ quadrant is closely identified with silicate and carbonate mineral dissolution/ precipitation, which, in turn, depends on groundwater velocity and supply of CO₂-charged meteoric water. Carbonate mineral dissolution/precipitation is comparatively rapid, though not as fast as dispersion of aerosols, but reactions involving aluminosilicates are much slower. The CARB group is prominent here, and, because of the importance of the Hunter River in the floodplain provinces, the HFP1 and HFP2 provinces are similarly included. The $(-Y_1, +Y_2)$ quadrant is dominated by the process of diffusion of connate salts from the WI2 province (molecular diffusion is the slowest known process in hydrochemistry). Oxidation of sulphides is the most important factor in the $(-Y_1, -Y_2)$ quadrant, which contains most samples from the GM group.

The mixing zone centred about the mean (Y_1, Y_2) score at the origin is of most interest for management of groundwater quality in the upper Hunter River valley. In this field all four of the major processes are represented to varying degrees, and the nature of their interaction is the subject of the next section.

Interpretation of non-reactive groundwater mixing by principal components

Some inferences can be made on the likelihood of significant groundwater mixing between subgroups of hydrochemical provinces by contrasting distances between canonical variate means (cf. Fig. 41), but it must be remembered that canonical variates analysis is a technique for discriminating group means only, since distance between individuals is not invariant under the canonical variates transformation. However, distance relationships between individuals are preserved in principal component scores from the pooled dispersion matrix, in this case the covariance matrix of standardised variates.

Figure 45a–d shows condensed plots of (Y_1, Y_2) scores from certain clusters of individuals in the central groundwater mixing zone (Fig. 44h). To avoid cluttering the diagrams with all the data points, the results are represented by elliptical envelopes which contain 95% of (Y_1, Y_2) scores for a particular hydrochemical province (Fig. 45a–d); the group mean scores are the centres of the ellipses, which are constructed so that the ratio of their semi-major to semi-minor axes is equal to the ratio of eigenvalues $(\lambda_1/\lambda_2)^{1/2}$ of the pooled correlation matrix.

Locations of significant groundwater mixing in the study area may be identified by the proximity of individuals to their own group mean score, as compared to their closeness to other group mean scores. In effect, Y_1 and Y_2 are now serving as linear discriminant functions for hydrodynamic mixing.

Undoubtedly, groundwater mixing is of most consequence in the Hunter River floodplain alluvium. In Figure 45a the HFP1 ellipse has been partitioned into five segments, of which four represent likely mixing zones between groundwater of the alluvium and the adjacent Permian fractured-rock provinces, on the basis of distance between individuals and group means; the remainder contains the samples which are hydraulically connected to the Hunter River and whose scores are closely identified with the source areas of the CARB–TRIAS province. Significant inflows of GM-type water are evident from the Hilliers Creek valley and from the Aberdeen and Hunter Thrust Faults. The Bayswater Seam subcrop coincides with the zone of inflow of WI1 water where it intersects the river below Ramrod Creek (Fig. 45a); in these areas the trace of the Bayswater Seam defines the WI1–WI2 boundary (Pl. 2). The WO province signature is prominent in the distal wells of the 'K' traverse drilled by Williamson (1958) above Denman (see Plate 2).

In the HFP2 group (Fig. 45b), the cluster of wells at Neotsfield, on the eastern edge of the study area, plots within the GM mixing zone, which suggests that the syncline between the Belford Dome and Sedgefield Anticline is a permeability barrier that induces upward leakage of groundwater from the Maitland Group rocks into the floodplain alluvium.

Inflow of WI2 type groundwater occurs in five wells on the southern side of the Hunter River at Alcheringa. The distribution of principal component scores of these wells (Fig. 45b) shows that the intensity of the WI2 signature decreases away from the confluence with Saddlers Creek, indicating that the most likely source of the WI2-type groundwater input is the Saddlers Creek valley, with the groundwater probably upwelling along fractures parallel to an anticlinal axis that is collinear with Saddlers Creek; however, the mixing zone might also be related to the triple junction of the Mount Coricudgy Anticline, Mount Ogilvie Fault, and Saddlers Creek Anticline. This mixing zone is one of the few in the entire floodplain that transects the Hunter River; everywhere else the river appears to be a true dividing streamline for groundwater flow. The Hunter River traverses the coal seams of the Malabar and Mount Ogilvie Formations of the Wittingham Coal Measures at Jerrys Plains, and the principal component scores of the HFP2 wells in this region indicate accession of WI2-type groundwater (Fig. 45b). However, downstream from Jerrys Plains to Neotsfield, aquifer storage and replenishment of low-salinity water from tributary streams such as Wollombi Brook and Glennies Creek are sufficient to generate (Y1, Y2) scores which plot within the CARB-TRIAS background field.

High-Cl⁻ groundwater inputs from the W11 province seem to emanate mostly from the Denman Formation at the top of the Wittingham Coal Measures. In the HFP2 province, a base-flow sample (number 263, bed underflow water) in Appletree Creek at its junction with the Hunter River plots in this field; the source was probably a spring flowing from the Denman Formation nearly 1 km upstream. There are many such saline springs along the contact between the Wollombi and Wittingham Coal Measures on the southern footslope of the valley between Alcheringa and Wambo Creek. During drought conditions in August–September 1982, most springs had ceased to flow, but numerous small-scale salt scalds testified to their activity in wetter times.

Principal component scores of samples at the confluence of Martindale Creek and the Hunter River form two discrete clusters (Fig. 45b). Surface samples and well water which are in hydraulic continuity with the Hunter River show a strong WO-type input, thus reflecting the influx of Goulburn River water. Wells closer to Martindale Creek plot near the TRIAS province mean, indicating that there may be substantial piping of Triassic groundwater along a lineament of the Mount Rombo spur.

In the WO province (Fig. 45c), inflow of WI2-type groundwater occurs in wells adjacent to Sandy Creek and in a meridional band in the Dalswinton area. Apparently, the alluvium of Sandy Creek intercepts saline water from the Mount Ogilvie Fault zone and transmits it downstream by bed underflow, and this water may be dispersed radially where intercepted by the cone of depression of pumping wells. However, the WO–WI2 mixing zone at Dalswinton cannot readily be explained and must be related to an unknown geological structure, probably associated with the Mount Ogilvie Fault.



Figure 45. Discrimination of zones of hydrodynamic mixing of upper Hunter River valley groundwater by principal component scores. Based on six \log_{10} -transformed variables of 670 individuals. Principal components from pooled correlation matrix. Mean scores of hydrochemical provinces shown. a — HFP1, b — HFP2, c — WO, d — WI1.



Figure 46. Hydrochemical trends by principal component scores of baseflow water in some upper Hunter River valley streams. a, b — domains whose water has reached or exceeded equilibrium with respect to certain minerals shown. c — Clustering by second and third principal component scores of facies variations for 670 samples of upper Hunter River valley groundwater. Clusters enclose at least 80% of scores for the hydrochemical subgroup shown.

Some bores and deeper wells of the WO group in localised groundwater discharge zones in the south and west of the study area intercept water which has a significant WI1 signature (Fig. 45c). At the scale of this investigation, it is not possible to be more specific on the origin of this water; however, it is likely that most of the dissolved salts are contributed by upwards flow from the Denman Formation.

Non-reactive groundwater mixing zones of the WI1 province are shown in Figure 45d. Similar zones are unlikely to be detected for the WI2 and GM groups, because of the inherently high salinity of these groups, which overprints the discriminatory power of $Y_1(R_p)$. The only detected zone of mixing between GM and WI1 province groundwater occurs in wells of the Dart Brook valley adjacent to Maitland Group rocks. Water with a WI2 signature occurs in the lower Spring Creek and Sandy Creek valleys and seems to emanate from saline groundwater of the Mount Ogilvie cross fault. Other WI1–WI2 mixing zones are indicated in areas of vertical upwards flow in the Wollombi valley and may in part be 'overspill' induced by structural impedance of the lateral transmission of groundwater by the Mount Thorley Monocline.

Perhaps the most significant of the WI1–WI2-type groundwater mixing zones is the western limb of the Muswellbrook Anticline, in particular the Saddlers Creek valley (Fig 45d). This result accords well with the HFP2–WI2 groundwater mixing zone across the Hunter River at Alcheringa, and adds credibility to the hypothesis of a likely major geological dislocation as the plane of transmission of upwelling WI2 groundwater.

The principal components of hydrochemical trends and equilibria

Figure 46a-b shows the $(Y_2(R_p), Y_3(R_p))$ scores of individuals whose water has simultaneously reached or exceeded saturation with respect to gypsum, amorphous silica, and chalcedony, and all three of the complex carbonates (dolomite, huntite, and hydromagnesite) considered earlier in the equilibrium calculations. The domains shown in Figure 46c are envelopes which enclose at least 80% of (Y_2, Y_3) scores for a particular hydrochemical subgroup, but they may also contain points from other subgroups. Since the second and third principal components together account for only 21% of total variance, the (Y_2, Y_3) plots are not particularly well suited for use as a clustering technique. As explained previously, $Y_2(R_p)$ and $Y_3(R_p)$ compare individuals by hydrochemical facies and are thus explicitly independent of total soluble salts; however, there is an indirect size dependence in their interpretation. In the high-salinity groundwater of the Permian fractured-rock provinces, $+ Y_2(R_p)$ is identified with the evolution of diffused connate 'marine' fluids, whereas, in lower salinity groundwater of the TRIAS, WO, and CARB provinces groups, it is a measure of the rapid dispersion of the univalent ions in aerosols transmitted by infiltrated rainwater; the $-Y_2(R_p)$ 'continental' association describes sulphide oxidation in high salinity water and is linked with slower dispersion of the divalent ions, particularly SO_4^{2-} , in low-salinity water. $Y_3(R_p)$ polarises the $HCO_3^{-}-Ca^{2+}-(Mg^{2+})$ 'continental' association of silicate and carbonate mineral dissolution/precipitation reactions against the SO_4^{2-} -Na⁺-(Cl⁻) 'marine' association, a secondary measure of diffusion of connate salts based on the sulphate residual.

The $(+Y_2, +Y_3)$ quadrant essentially partitions the sample space into four hydrochemical facies, each of which is associated with distinct mineral equilibria fields, some of which are shown in Figure 46a–b. This quadrant is primarily identified with maturation of groundwater with significant diffused connate marine salts, and is secondarily linked with silicate and carbonate mineral dissolution/precipitation; from the proportion of its area saturated and supersaturated with respect to silica and the complex carbonates, it is evident that precipitation dominates. The west limb of the Muswellbrook Anticline has the greatest proportion of samples in this quadrant, indicating that both of the above hydrochemical processes are the most important factors in this subgroup. The $(+Y_2,-Y_3)$ quadrant is most closely identified with the 'marine' Na⁺-(Cl⁻) ion association, and points distal to the origin bear the signature of diffusion of immature connate marine water and saturation with respect to the complex carbonates. This quadrant contains the largest proportion of WI2 samples, in particular those from the Wollombi Brook valley. Points that plot in the $(-Y_2, +Y_3)$ quadrant represent areas where the 'continental' processes of silicate and carbonate mineral dissolution/precipitation and/or sulphide oxidation are dominant. The key major elements are Ca^{2+} and (Mg^{2+}) ; most of the HFP1 and HFP2 samples are located here. A minor proportion of samples in this quadrant have attained silica saturation, but it is clearly evident that mineral dissolution rather than precipitation dominates. The $(-Y_2, -Y_3)$ quadrant segregates the high-sulphate water of the GM and WI2 provinces, and contains the gypsum saturation field.

The relationship between groundwater facies, mineral equilibria, and hydrochemical trends will now be considered using principal components. Ideally, hydrochemical trends are best traced by sequential sampling in the same aquifer along groundwater flow lines; however, such arrangements of sampling points were not available in the study area, the nearest alternative being the base-flow measurements, some of which are plotted in Figure 46a–b.

The headwaters of Martindale Creek, Spring Creek, Doyles Creek, and Wollombi Brook drain the TRIAS province and then flow through the WO province. Within these provinces the loci of the four streams (equated here with groundwater flow lines) generally show the same trend of continuous increase in Cl^{-} and HCO_{3}^{-} concentrations in roughly the same proportions: if this process were to be continued uninterrupted, the water would ultimately reach the silica and complex-carbonate saturation fields in the $(+Y_2, +Y_3)$ quadrant. However, in the Wollombi Brook samples, (Fig. 46b) the TRIAS-WO trend is reversed upon interception of solutes from the Wittingham Coal Measures, and the concurrent increases in Cl-, Na+, and SO_4^{2-} and decline in HCO₃ rotate the locus back towards the -Y₃ axis, which is a measure of the diffusion of connate marine salts. In Spring Creek (Fig. 46b), the locus is rotated 90 across the Mount Ogilvie cross fault, and the trend is then towards the WI1 province domain associated with diffusion of juvenile connate water.

Glennies Creek, Muscle Creek, and Bowmans Creek baseflow samples show the same trend of decreasing Y_2 and Y_3 scores towards the gypsum saturation field as Cl⁻ increasingly dominates over HCO_{3}^{-} , and SO_{4}^{2-} concentrations progressively increase with distance away from the CARB province in the Permian fractured-rock provinces of the Central Lowlands. The trend towards gypsum saturation in Bowmans Creek (Fig. 46a) is perturbed at station 126 by an input of Na⁺-Cl⁻ water, which rotates the locus towards the WI2 domain; however, on subsequent mixing with local groundwater further downstream the locus reverts back towards gypsum saturation. Since water quality of the Hunter River is of critical importance in the region, its locus is included in Figure 46a, but it is acknowledged that the points defining its locus cannot be directly related to groundwater flow lines in the adjacent Permian rocks, because of the regulated flow component in the river. Above Denman, the Hunter River locus shows a similar trend to the TRIAS-WO province base-flow loci. There is a marked facies change at Denman, which reverses the locus towards the direction of the CARB-Permian province streams. Inflow and mixing of Goulburn River water results in a compensating facies change back towards the value of its original position above Denman, but displaced further along Y₂ towards the silica, and complex-carbonates saturation fields. From the Goulburn River confluence to Jerrys Plains, the Hunter River locus again reverts to the CARB–Permian province trend, reflecting accession of groundwater seepage from the Wittingham Coal Measures. There is a minor facies change between Jerrys Plains and the Bayswater Creek–Singleton section of the river, where the lower Y_3 scores mainly result from disproportionate decreases in HCO₃⁻ concentration.

Sandy Creek and Saddlers Creek (Fig. 46a) both drain the WI1 province. Unlike the trends shown by the TRIAS-WO and CARB-Permian province streams, sequential WI1 base-flow samples show far greater variation along Y_2 and Y_3 . This indicates the importance of diffusion of connate juvenile water of Na^+ -HCO₃ facies in groundwater of the WI1 province. In contrast, the trend of the loci of WI2 groundwater flow lines, represented here by base flow in Loder Creek (Fig. 46a), is dominated by the diffusion of immature connate 'marine' water, which accounts for the trend towards the Na⁺-(Cl⁻) facies of the $(+Y_2,-Y_3)$ quadrant. The solutions are not concentrated enough to reach halite saturation, but the domain represented by stations 54, 57, and 55 (Fig. 46a) is supersaturated with respect to the complex carbonates (Q_{huntite}>2.5, $Q_{hydromagnesite} > 2$, $Q_{dolomite} > 3$). On intersecting the Maitland Group rocks, the Loder Creek base-flow locus is rotated

From a combination of graphical techniques, chemical equilibrium models, and multivariate statistical methods, it has been possible to discriminate the various hydrochemical processes which exert the greatest influence on groundwater chemistry in the upper Hunter River valley. Based on geological differences, the system is partitioned into eight provinces, each with a unique hydrochemical signature.

The fractured rocks of the southern New England Fold Belt constitute the CARB province, characterised by groundwater of low to moderate salinity (mean TSS = 790 mg/L) which grades from $Ca^{2+}-Mg^{2+}-HCO_3^-$ facies to Na⁺-Cl⁻ facies towards the Hunter Thrust Fault, thus reflecting the increase down flow lines of solution of locally redistributed cyclic salts over silicate mineral dissolution.

The TRIAS province comprises the scarp-forming fractured rocks of the Triassic Narrabeen Group in the south and west of the study area, and their associated groundwater. The groundwater is of low to moderate salinity (mean TSS = 600 mg/L), and dominated by Na⁺–(Mg²⁺)–Cl⁻. HCO₃⁻ concentration is generally low, because groundwater throughflow is rapid and the soil cover shallow and depleted in organic matter, and the major source of dissolved CO₂ in recharge water is atmospheric.

The Permian fractured rocks forming the Central Lowlands and footslopes have been divided into four provinces, namely, WO, WI1, WI2, and GM1. The WO province consists of groundwater of the Wollombi Coal Measures, which occupy the footslopes below the Triassic escarpment. WO-type groundwater is moderately saline (mean TSS = 1070 mg/L), dominated by Na⁺, Mg²⁺, Cl⁻, HCO₃⁻. The hydrochemical processes which have most influence on the composition of WO-type groundwater are oxidation of coal seams and silicate mineral dissolution in the abundant tuffaceous interseam beds. The fundamental difference between the Wollombi Coal Measures and the underlying Permian rocks is that the latter were periodically submerged by oceanic water at various stages of diagenesis; to this day, the solute inputs from these marine transgressions have a profound influence on the groundwater chemistry of the Permian fractured rocks of the Central Lowlands.

towards gypsum saturation. Base flow in other streams draining the Loder Dome, such as Nine Mile Creek and the east arm of Loder Creek, shows the same trend (Fig. 46a).

In summary, the facies changes shown by (Y_2, Y_3) scores of base-flow samples are probably a reasonable approximation to hydrochemical trends along groundwater flow lines in the provinces drained by these streams. Flow lines emanating from the Triassic escarpment show increased sensitivity to 'continental' Y₃ processes of silicate and carbonate mineral dissolution reactions as groundwater velocity declines through the Wollombi Coal Measures. Conversely, flow lines in the Wittingham Coal Measures show progressively decreasing Y₃ scores in the WI2 group, and progressively increasing Y₂ scores in the WI1 province - a consequence of the maturity of diffused connate marine salt solutions and the fact that carbonate precipitation dominates over carbonate dissolution within these provinces. Flow lines in the GM province converge towards gypsum saturation by concurrent decreases in Y_2 and Y_3 scores. It is interesting to note that facies changes interpreted from (Y₂, Y₃) plots (Fig. 46c) are generally much more pronounced than those obtained by visual inspection of base-flow longitudinal profiles (cf. Wollombi Brook; Figs. 15b and 46b) or even by the use of conventional trilinear diagrams, since the method associated with the latter loses two degrees of freedom by using ionic proportions.

SYNTHESIS

Groundwater of the Wittingham Coal Measures is divided into that of the intruded rocks of the Jerrys Plains Subgroup in the west, which form the WI1 province, and water of the nonintruded rocks of the WI2 province in the eastern and southeastern parts of the study area. WI1 groundwater is of moderate to high salinity (mean TSS = 2300 mg/L), whereas water of the WI2 province is the most saline in the Hunter River valley (mean TSS = 5700 mg/L). Hydrochemical facies grade from Na⁺, Cl⁻, HCO₃ in the WI1 province to Na⁺-Cl⁻ in the WI2 province, and mean SO₄²⁻ concentration is over ten times higher in the WI2-type groundwater. The lower average salinity and different chemical composition of the WI1-type groundwater are a consequence of both a longer period of flushing by meteoric water and prior thermal mobilisation of connate marine fluids peripheral to the Tertiary intrusives.

The GM province consists of groundwater of the Maitland Group, Greta Coal Measures, and Dalwood Group, and therefore incorporates the largest proportion of marine sedimentary rocks in the study area, as reflected in the chemistry of its water, which is dominantly Na⁺, Mg²⁺-Cl⁻, SO₄²⁻ facies and highly saline (mean TSS = 4300 mg/L). The strong marine signature is perpetuated through the upper seams of the Greta Coal Measures because these beds were saturated by oceanic water while they were still actively growing peats.

The largest groundwater storage in the upper Hunter River valley is in buried sand and gravel of the floodplains. These sediments are by far the most permeable aquifers, and their water quality is of critical importance to irrigation activity. During drought conditions in August 1982, there was considerable withdrawal of groundwater from wells in the floodplain; this pumping induced surface recharge in areas peripheral to the Hunter River, but resulted in the deterioration of water quality in some outlying areas that were not in direct hydraulic continuity with the bed underflow water of the river. The floodplain is divided into the HFP1 and HFP2 provinces; the boundary between the two is the Hunter-Goulburn River confluence, which marks a distinct break in mean grainsize, sorting, and provenance of the aquifers, separating the coarsegrained lithic sediments derived from the Carboniferous rocks in the HFP1 province from the fine-grained dominantly

quartzose sands eroded from the Triassic rocks in the HFP2 province. In terms of hydrochemical facies, the HFP1 and HFP2 provinces are similar, with Mg^{2+} dominant over Na^+ in HFP1 type groundwater, grading to Na^+ dominant over Mg^{2+} in HFP2 groundwater; HCO_3^- and Cl^- , in that order, are the most abundant anions in both groups. However, increased contact time with the Permian rocks results in an increase in mean TSS from 650 mg/L in the HFP1 province to 840 mg/L in the HFP2 province.

Over the total sample space of 673 individuals, HCO_3^- , Ca^{2+} , and aqueous SiO_2 concentrations approach log-normal distribution, and can therefore be considered as the products of many small interdependent causes in a statistically homogeneous system characterised by dissolution/precipitation reactions and ion exchange under a continental leaching environment. In contrast, log_{10} -transformed SO_4^{2-} , Na^+ , Mg^{2+} , and Cl^- concentrations approach bimodal distribution, and it is no coincidence that these four elements together constitute over 97% of dissolved ions in ocean water. As a simplistic overview, the low concentration modes of the SO_4^{2-} , Na^+ , Mg^{2+} , and Cl^- distributions can be considered with HCO_3^- , Ca^{2+} , and SiO_2 as representing the dissemination of 'elements' from the continental solute store, whilst the high concentration modes of the former four elements are a legacy of the Permian marine transgressions.

The dominance of modern continental processes over relict marine influences is indicated by the pattern of solute behaviour within the hydrochemical provinces. The highest rates of HCO3 enrichment relative to Cl⁻ are attained in the CARB and TRIAS provinces, a consequence of carbonate and silicate mineral dissolution by aggressive water in the recharge zones. Similar high rates of $HCO_{\overline{3}}$ accretion occur in the WO and WI1 provinces, which partly reflect active leaching in the higher parts of the valley floor, although the groundwater probably also contains a component resulting from solution of silicates in the dolerite intrusions. The effects of an additional source of HCO₃ from oxidation of coals by sulphates in the reducing zones of the WI2 and GM provinces is more than offset by the increased potential for carbonate mineral precipitation, and therefore significantly lower rates of HCO3 enrichment occur in these provinces. The HFP provinces also record low rates of HCO3 enrichment relative to Cl- -— an expression of the conservative behaviour of Cl⁻ compared to $HCO_{\overline{3}}$ along flow lines converging towards the groundwater sinks of the floodplain — and it is also likely that some $HCO_3^$ losses occur from degassing as the semi-confined aquifers of the Permian fractured rocks discharge into the phreatic aquifers of the floodplain.

The behaviour of aqueous SiO₂ relative to Cl⁻ shows that the Permian fractured-rock provinces separate into the WO and WI1 groups. The dominant continental influence of silicate mineral dissolution results in linearly increasing SiO₂ concentration along flow lines; in contrast, the WI2 and GM groups with strong relict marine influences are characterised by decreasing silica solubility along flow lines as Cl⁻ concentration increases by molecular diffusion. In particular, the Muswellbrook-Denman-Jerrys Plains triangle is segregated on the basis of high SiO2:Cl- ratios, and this area probably represents a zone of maximum intrusive activity. The same clustering of the Permian fractured-rock provinces is attained by trends in the SO₄²⁻:Cl⁻ ratios. The WO and WI1 provinces have a significantly lower rate of SO_4^{2-} enrichment down flow lines than have the WI2 and GM provinces. In this case, trends within the WO and WI1 provinces mostly reflect the systematics of SO_4^{2-} derived from the continental sulphate store, and represent processes ranging from infiltration of aerosols in contemporary rainfall to dissemination of terrigenous sulphate accumulated in the WO and WI1 peat swamps; however, there was also an input of oceanic sulphate during the brief marine transgression represented by the Denman Formation, par-

ticularly in the southern part of the study area. The strong marine signature in the WI2 and GM provinces is represented by the high rate of SO_4^{2-} accretion along flow lines, the combination of molecular diffusion of primary SO_4^{2-} in connate marine salts, and oxidation of sulphides. No acid water associated with pyrite oxidation was detected during the survey, because in the undisturbed environment the change in pH induced by acids released from the oxidation reaction is buffered by HCO₃, which may be concurrently produced by dissolution of authigenic carbonate. However, in spoil heaps this buffering mechanism will not operate if the critical fluid transmission rate lies between the pyrite oxidation and carbonate dissolution reaction rates.

Calculation of Disequilibrium Indices for minerals which have precipitated under past and present groundwater regimes in the upper Hunter River valley permits broad comparison to be made between palaeohydrochemical environments and the present one. Saturation and supersaturation with respect to the simple carbonate minerals calcite and magnesite is the norm in groundwater of the floodplain and fractured rocks of the Central Lowlands. However, the validity of equilibrium models for those parts of the alluvial system which are in direct hydraulic continuity with the Hunter River is questionable: because of the comparatively high groundwater velocity, perhaps groundwater-mineral relationships in the alluvial aquifers would be more suitably analysed by rate kinetics. The abundance of calcite precipitates in the contemporary hydrochemical system is manifest in the ubiquitous calcite joint and cleat linings in the Permian coals and interseam beds; its former presence is recorded by the calcite cements and older planar void infills in these rocks. Magnesite is slightly more soluble than calcite, but has not been reported in the study area - the available CO_3^{2-} after precipitation of complex carbonates is apparently all consumed by calcite. In contrast to the high potential for calcite precipitation in groundwater of the Central Lowlands, it and other Ca-Mg minerals would be dissolved in contact with most water in the TRIAS and WO provinces in the southern and western recharge zones, but not by water of the CARB province in the northern recharge zone.

The former abundance of siderite in groundwater of the upper Hunter River valley is indicated by its presence as a cement and replacement mineral throughout the Permian rocks, particularly in the terrigenous sequences. However, on chemical considerations siderite must be classified as a product of a palaeohydrochemical regime, since there is simply not enough dissolved Fe^{2+} in the present groundwater of the study area for siderite precipitation to be significant on a regional scale. Corroborating petrographic evidence indicates that siderite formed during early diagenesis. Solubility of Fe²⁺ and Al^{3+} is greatly increased in acid water, hence the Permian peat swamps would have been important zones of accumulation for these elements. Both Fe^{2+} and Al^{3+} have subsequently been lost to the system in oxyhydroxides, but Al^{3+} has also been consumed by precipitation of the rare complex-carbonate mineral, dawsonite. Disequilibrium Indices show that dawsonite precipitates in the contemporary hydrochemical system in the upper Hunter River valley. The petrologically determined range of dawsonite as an authigenic mineral spans the period from early diagenesis to the present, which implies that the palaeohydrochemical environment was also characterised by alkaline water rich in Na⁺ and Al³⁺. However, the mechanism responsible for the concurrent removal of SiO₂ from solution in order to prohibit kaolinite precipitation is not fully understood.

Although halite, thenardite, and bloedite commonly occur in salt efflorescences throughout the WI2 and GM provinces, the groundwater in these provinces is grossly undersaturated with respect to these minerals. Similarly, glauberite would be dissolved by all of the groundwater samples in this data set, and it is therefore not surprising that primary glauberite is never observed in the Permian rocks. On the other hand, pseudomorphs of calcite, dolomite, and dawsonite after glauberite could have formed at any diagenetic stage, because groundwater of the Permian marine sequences is supersaturated with respect to these minerals, and presumably has always been so. Gypsum pseudomorphs are more time-specific, since there is no water in this data set capable of precipitating gypsum; however, there are several samples in the GM province which are in equilibrium with gypsum.

The very narrow range of Disequilibrium Indices for chalcedony and amorphous silica shows indirectly that the solubility of these minerals controls silica concentration in the upper Hunter River valley groundwater.

Models based on incongruent dissolution of K-feldspar and Ca-plagioclase allocate much of the region's groundwater to the kaolinite stability field, a result which is consistent with the observed abundance of kaolinite as an authigenic mineral in the Permian coals and other fractured-rock aquifers. Silica and cations leached from the fractured rocks of the valley accumulate in the groundwater sinks around the low permeability margins of the HFP2 province because this area has the largest proportion of water in equilibrium with Ca-montmorillonite. However, in the model for incongruent dissolution of Na-plagioclase, sample points are generally evenly dispersed about the albite-kaolinite boundary, which suggests that albite would not be dissolved by about half of the groundwater samples in this data set, particularly the sodium-rich water of the WI2 and GM provinces. Stability diagrams are only useful in describing the genesis of water if dissolution of a particular mineral and its weathering products represents a substantive source of the ions forming the axes of the diagram. In this regard, we consider that, in terms of aluminosilicate groundwater equilibrium, the maturity of the upper Hunter River valley groundwater is best explained by the K-feldspar and Caplagioclase stability diagrams, since silicate dissolution represents an important source of both K⁺ and Ca²⁺ in this system. Conversely, dissolution of sodic plagioclase is only an important process for Na⁺ enrichment in those samples that constitute the low-concentration mode of the distribution of Na⁺ in this system; samples in the high-concentration mode are highly identified with diffusion of connate marine salts.

The interaction between modern continental hydrochemical processes and marine connate salts in the upper Hunter River valley fractured-rock aquifers is a recurring theme throughout this study; the interaction of these processes is illustrated in Figure 43. This concept is introduced on a regional scale by comparing the distribution of the 'continental elements' - K^+ , Ca^{2+} , SiO₂, and HCO₃ — against distribution of the four major 'elements' constituting the bulk of dissolved solids in ocean water - Cl⁻, Na⁺, SO₄²⁻, and Mg²⁺. On a provincewide scale, composition diagrams of solute behaviour identify the WI2, GM and, to a lesser extent, WI1 provinces as systems that can be approximated by simple linear mixing models between meteoric and oceanic water. At the other end of the spectrum, the floodplain provinces can be considered as mixing systems between Hunter River surface water and groundwater of the fractured-rock provinces. Salt efflorescences are the surface expressions of the strong association between inherent marine solutes and the provinces comprising the Wittingham Coal Measures and the older Permian rocks in the Central Lowlands; in particular, the Mulbring Siltstone of the GM province is the unit most closely identified with surface salting

— the Wollombi Brook valley appears to be the most saltaffected area in the upper Hunter River valley. The subsurface expression of the link between marine solutes and the older Permian fractured-rock provinces is represented by the accretion of Na⁺, Cl⁻, and SO₄²⁻ along groundwater flow lines, and is equated in this report with sequential base-flow measurements along certain streams during the drought conditions in August 1982.

Inferences about the relative strength of continental and relict marine influences on the chemistry of the upper Hunter River valley groundwater are put onto a quantitative footing by the use of multivariate statistical methods. The two techniques used in this study are related in the following way: the principal components measure several independent directions of evolutionary change in upper Hunter River valley groundwater, whereas the canonical variates show how far the evolutionary processes have progressed to the present time. Thus, after the variation due to size effects is removed, $Y_2(R_p)$ compares the strongest 'marine' influence of diffusion and maturation of connate water against the strongest 'continental' process of sulphide oxidation; separation of group means along the second canonical vector indicates that diffusion of Na⁺-Cl⁻-type groundwater is the dominant 'marine' signature in the Wittingham Coal Measures, and sulphide oxidation is co-dominant with diffusion of connate marine salts in the GM province. $Y_3(R_n)$ compares the next most prominent 'continental' process of silicate and carbonate mineral dissolution/precipitation reactions against a secondary measure of diffusion of connate marine salts, based on the relative mobility of SO₄²⁻ and Cl⁻ ions. Likewise, the third canonical variate contrasts group means according to the intensity of silicate and carbonate mineral dissolution/precipitation reactions, and also emphasises the importance of ion mobility effects.

The hypothesis that geological provenance is the dominant control on the chemistry of the upper Hunter River valley groundwater has been tested by regrouping the data into smaller subsets, which incorporate geographic variation and differences in the mode of transmission, and then subjecting the subgroups to a second canonical variates analysis. The integrity of the grouping by geological provenance is maintained through the second canonical variates analysis, thus showing that geology is the dominant factor. On the scale of individuals, groundwater mixing zones are identified by the discrimination of hybrids according to their first and second principal component scores. In this survey several important mixing zones have been identified, but there may well be others undetected in areas of limited data coverage. In the floodplain provinces, significant input of GM-type groundwater emanates from the Aberdeen and Hunter Thrust Faults, the Hilliers Creek Valley, and the Neotsfield area to the east of Singleton. Input of WI2-type groundwater occurs at Jerrys Plains and Alcheringa; the latter mixing zone is of special significance, because the source is sufficiently strong to overprint the role of the Hunter River as a dividing streamline for groundwater flow. Perhaps the strongest source of WI2type groundwater is upwelling along the Mount Ogilvie Fault. Input of this water into the TRIAS and WO systems is reflected by saline pulses in base-flow chemistry of Big Flat Creek and Spring Creek, and its dispersion through the local groundwater is shown by the shift in principal component scores of bores and wells in the lower sections of the valleys drained by these streams.

DISCUSSION

The sources of saline groundwater in the upper Hunter River valley are the GM, WI2, and, to a lesser extent, WI1 provinces. Within these provinces, the fine-grained marine sediments of the Mulbring Siltstone, Bulga Formation, and Denman Formation represent the strongest primary sources of marine solutes. However, groundwater disseminated from these units tends to be most saline towards the south of the study area, in the Wollombi Brook valley.

There also appears to be a trend of soluble salts increasing with the age of these units, reflecting a higher degree of leaching by meteoric water in units nearer the land surface. From the spatial variation in salinity it might be inferred that the Wollombi Brook valley to the south is a younger geomorphic surface than the main Hunter-Goulburn River valleys, but it might also be an expression of distance from Permian shorelines. Sulphur isotope studies (Smith & Batts, 1974) and trace element analyses (Swaine, 1962) have established that the upper seams of the Greta Coal Measures and the Vane Subgroup were enriched in marine solutes by direct contact between transgressing marine water and the growing peats. Accretion of marine solutes in buried coals would have occurred at a slow rate by downwards diffusion. the depth of penetration of the solute front being dependent upon the duration of the marine transgression, depth of ponding, and rate of sedimentation on the sea floor.

The fact that Permian marine solutes are still diffusing out of rocks in the study area requires some explanation. Firstly, the opportunity for convective and dispersive flushing of connate marine fluids has existed only since Tertiary uplift created the appropriate difference between the high potential of the uplifted Upper Hunter dome belt and the low potential eastwards towards the coast. In the intervening period, the Permian rocks were at or below mean sea level, and it is quite feasible that brines may have accumulated at depth during this period. The groundwater flux out of the upper Hunter River valley system in the early stages after uplift would have consisted of Na⁺-Cl⁻-SO₄²⁻-rich water of far higher salinity than modern groundwater outflow. In particular, early drainage water from the Mulbring Siltstone would have transported solutes derived from glauberite and halite dissolution, neither of which exists as a primary mineral today, and Na⁺, Cl⁻, and SO_4^{2-} concentrations exceeding those of sea water may well have been attained along flow lines of deep circulation. The present brittle fracture system in the Permo-Triassic rocks developed in response to uplift and erosional unloading, and resulted in enhanced fracture permeability in the coals relative to the interseam beds. In the contemporary Permian fracturedrock system, groundwater flow lines are strongly refracted about the coal-sediment interfaces, and most groundwater is preferentially transmitted along the path of least hydraulic resistance, (viz. the conduits formed by an interconnected network of cleats and bedding plane separations in the coal seams). Geochemical studies in the Wollombi Brook valley indicate that there has been translocation of salts from the coal seams into the reservoir rocks of the adjacent coarse-grained sediments. The convective component of this process would have been exhausted long before Tertiary uplift, and represents lateral expulsion of interstitial fluid from the coals, owing to consolidation and decreasing porosity with rank advance, the greatest decrease in porosity occurring during early coalification. Porosity of the bituminous coals in the upper Hunter River valley now averages around one-tenth of that of the original peats.

Molecular diffusion is therefore the only hydrochemical process which is sufficiently slow to explain the persistence, from Tertiary uplift to the present, of marine solutes in the active leaching regime of upper Hunter River valley groundwater. The Wollombi Brook valley geochemical studies show that the current status of the system, in that area at least, is described by molecular diffusion of solutes from the coal matrix towards the cleats and bedding-plane partings. In areas of unimpeded groundwater drainage to the north of the valley, particularly in the WI1 province, it may well be that solutes are being diffused from the interseam sediments towards the highly permeable coal fractures, but this process could only be established by detailed geochemical analyses. In the Mulbring Siltstone, molecular diffusion drives the marine solutes from the rock matrix towards tension fractures. The rate of diffusion depends on the concentration gradient between the rock matrix and the fracture; hence, if solute transport along fracture planes is impeded by factors such as structural boundaries or mineral precipitates on fracture faces, the rate of flux of solutes is considerably retarded. Both factors are operative in the WI2 and GM provinces in the Wollombi Brook valley. From principal components analyses it has been possible to discriminate the dimension associated with molecular diffusion of connate marine salts; for similar positions along flow lines in groundwater discharge zones, WI1-type groundwater is only at the juvenile stage, and WI2 and GM-type waters have not advanced past the immature stage of the evolutionary sequence $Na^+-Cl^- \longrightarrow Na^+-HCO_3^- \longrightarrow Ca^{2+}-HCO_3^-$, despite active circulation of groundwater in this system since Tertiary uplift. Therefore, in planning for future development in the upper Hunter River valley, it should be recognised that high background salinity in groundwater of the Central Lowlands is a natural phenomenon which will persist for the foreseeable future.

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