

5. HYDROCHEMISTRY OF GROUNDWATER IN THE CALIVIL FORMATION

5.1 Introduction

The hydrochemistry discussed here is restricted to the regional groundwater passing down the Loddon Valley deep lead system and contained within the Calivil Formation aquifer. The area covered extends from Moolort, in the central Loddon Valley within the highlands, out across the Loddon Plain to Mincha West in the north of the plain, a distance of about 150 km. The salinity profile (Figure 5.1) along the section shows that the groundwater within the highlands is about 1,000 to 1,200 mg/l. rising to about 2,300 mg/l across the southern Loddon Plain, but then climbing rapidly to over 10,000 mg/l in the north of the plain prior to the junction with a Murray Valley system where salinities fall markedly (Figure 4.6c).

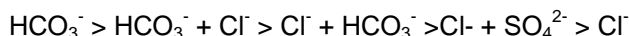
Individual ion activities and chemical equilibria data for the groundwaters of the Loddon Basin were calculated by means of the WATEQF computer program, a revised version of the WATEQ computer program (Truesdell and Jones, 1974). The program calculates the equilibrium distribution of 114 aqueous species in natural waters from their chemical analyses and gives the saturation state of the waters with respect to the various mineral phases.

WATEQF consists of a main program and 5 subroutines - PREP, SET, MODEL, PRINT and SAT. PREP reads the input water data (in this instance all data being provided as mg/l), converts the units to molality, and calculates all the temperature dependent data at the temperature of the water sample arbitrarily chosen as 20°C. SET initializes values of individual species for the iterative Mass Action - Mass Balance loop. MODEL calculates activity coefficients, PRINT prints the results calculated from the aqueous model, and SAT calculates and prints the thermodynamic saturation state of the water with respect to the various minerals considered by the program.

To assist in the examination of the chemical evolution of the groundwaters in the regional Calivil Formation aquifer, the program was run on 38 representative waters from localities along the Loddon Valley, from Glendaruel, south of Moolort in the highlands, to Mincha West in the northern Loddon Plain (Table 5.2).

5.2 Groundwater Classification

The general groundwater sequence along the Loddon Valley follows the classical sequence of Chebotarev (1955), who observed that all groundwaters tend to the composition of sea water. Chebotarev's sequence is



In order to have a quantitative framework to separate the categories, a modified version of Back's (1961) classification of hydrochemical facies has been adopted (Table 5.1).

TABLE 5.1 - Classification of hydrochemical facies*

Hydrofacies	Percentage of constituents in equivalents per million			
	Ca+Mg	Na+K	HCO ₃ +CO ₃	Cl+ SO
Cation facies:				
Calcium-magnesium	90 - 100	0 - 10		
Calcium-sodium	50 - 90	10 - 50		
Sodium-magnesium	10 - 50	50 - 90		
Sodium-potassium	0 - 10	90 - 100		
Anion Facies:				
Bicarbonate			90 - 100	0 - 10
Bicarbonate-chloride-sulphate			50 - 90	10 - 50
Chloride-sulphate-bicarbonate			10 - 50	50 - 90
Chloride-sulphate			0 - 10	90 - 100

Modified from Back (1961)

Chemical Analyses

The chemical analyses of water samples used in this study were carried out by the Department of Minerals and Energy's Chemical Branch at the Victorian State Laboratories, under the direction of Mr R Mealan, Deputy Chief Chemist. The following is a summary of the techniques used for chemical analysis.

TOTAL SOLUBLE SALTS: BY SUMMATION OF CATIONS AND ANIONS

Chloride:	Potentiometric titration with silver nitrate
Carbonate & bicarbonate:	Potentiometric titration with standard acid, using a pH electrode
Sulphate:	1. Precipitation as barium sulphate, determined gravimetrically 2. Turbidimetric, with barium chloride
Nitrate:	Ultra violet absorption
Calcium:	Atomic absorption
Magnesium:	Atomic absorption
Sodium:	Atomic absorption
Potassium:	Atomic absorption
Soluble iron:	Atomic absorption
Total iron:	Atomic absorption
Silica:	Colorimetric, using ammonium molybdate
Bromide:	Volumetric, oxidation to bromate, then titration with sodium thiosulphate

SG: Comparing mass of a known volume with distilled water

pH/Eh: While pH values were automatically recorded in the laboratory, where consideration is given to pH/Eh relationships - as throughout Chapter 7- measurements were taken in the field using a Titron k-240 portable pH/Eh meter. This meter contains a combined pH electrode, which reads on two scales, 0-8 and 6-14. Two electrodes were used for Eh measurements - platinum electrode and calomel reference electrode.

TABLE 5.2 - Hydrochemistry of Calivil Formation waters (mg/l)-Loddon Valley

Bore No.	TDS	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	SiO ₂	pH
Glendaruel 34	605	80		284	80	4	27	26	104	8.15
Neereman 10001	957	322	48	281	210	6	29	46	15	7.3
Neereman 10016	1049	273	1896	21	302	7	22	9	19	7.2
Moolort	902	216	90	316	136	6	39	61	38	7.85
Moorlort 8008	1026	260	96	342	231	-	27	43	23	7.4
Moolort 8009	1050	283	97	323	249	-	23	49	24	8.3
Baringhup 8002	866	259	27	329	153	-	45	53		7.5
Baringhup 10003	1232	441	79	305	256	8	42	66	36	8.0
Baringhup 10006	1315	456	68	357	238	8	58	85	45	7.5
Laanecoorie 51	1368	502	95	336	304	-	47	74	10	7.1
Laanecoorie 10001	1162	430	35	287	270	7	38	53	32	8.1
Bridgewater 17	1017	414	23	305	281	-	14	45	3	8.6
Bridgewater 8007	1161	480	76	305	331	-	27	53	26	7.0
Bridgewater 6	1196	460	67	282	306	-	27	51	1	7.5
Bridgewater 8008	1476	646	1038	20	390	-	27	66	35	6.9
Yarraberb 8005	1247	444	66	313	277	8	40	56	43	7.75
Yarraberb 10002	1382	546	79	282	357	9	38	49	22	8.5
Yarrayne 10010	1440	565	88	289	345	7	39	62	45	7.6
Pompapiel 1	1373	590	24	302	356	8	21	62	10	8.2
Pompapiel 8001	1688	729	110	526	418	8	43	75	32	7.8
Pompapiel 8013	1928	842	165	226	526	8	45	74	42	8.3
Janiember East 8004	1435	582	88	269	352	7	35	61	21	7.7
Janiember East 8014	1496	612	96	268	372	7	35	63	43	7.9
Janiember East 8008	1560	673	102	238	387	7	39	69	45	7.95
Janiember East 8007	1595	717	94	226	384	5	49	75	45	7.4
Janiember East 16	1572	769	39	218	440	7	17	78	3	8.3

Bore No.	TDS	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	SiO ₂	pH
Talambe 8001	2096	977	153	245	536	10	55	96	24	8.0
Calivil 8004	2155	999	162	256	552	9	58	97	22	7.6
Calivil 8003	2197	1034	146	248	570	9	63	105	22	7.2
Calivil 5	2266	1057	167	260	587	9	63	105	18	7.5
Calivil 9	2198	1039	165	244	570	9	63	103	5	8.2
Calivil 3	2303	1079	181	253	588	10	64	106	21	7.4
Calivil 8002	2307	1090	133	296	602	10	59	105	12	7.9
Mologa 1	6248	3350	357	322	1815	17	127	253	8	7.8
Mologa 2	6312	3330	407	317	1827	19	140	264	8	7.7
Mologa 8001	6050	3135	357	330	1804		107	213		7.3
Mincha West 12	9119	5112	678	70	2560	14	262	417	5	7.3

5.3 The Chemical Evolution of Groundwater in the Calivil Formation

Upstream of Bridgewater, recharge waters percolate downward through valley flow basalts (Chapter 4.1) prior to reaching the pebbly wash and quartz drift sand of the Calivil Formation. Of the basalts, the most common rock types are alkali olivine basalt and olivine tholeiite, for which chemical analyses are given in Table 5.3.

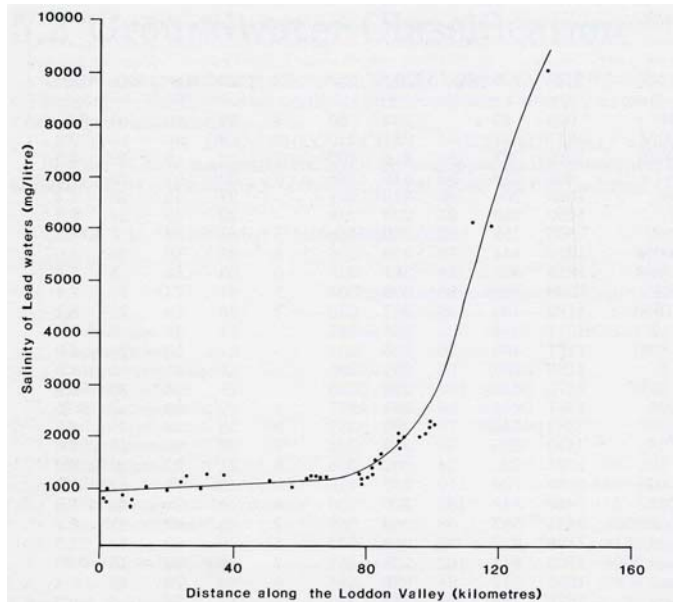


Figure 5.1 - Salinity variations in the Calivil Formation of the Loddon Valley between Moolort and Mincha West. The rapid rise in salinity commences virtually at the hinge line between the regional groundwater recharge and discharge zones in the Pompapiel district (see also Figure 4.6c).

TABLE 5.3 - Analyses of basalt types found in the upper Loddon catchments*

	Analysis 1	Analysis 2		Analysis 1	Analysis 2
SiO ₂	42.30	45.31	Orthoclase	8.51	8.27
TiO ₂	3.21	2.95	Albite	18.68	25.30
Fe ₂ O ₃	4.39	3.74	Anorthite	21.80	26.13
FeO	7.39	7.54	Diopside	17.12	12.10
MnO	0.18	0.17			
MgO	10.77	7.66			
CaO	9.46	8.87			
Na ₂ O	2.81	2.99			
K ₂ O	1.44	1.40			
P ₂ O	0.55	0.43			
H ₂ O	0.74	0.46			

Analysis 1 - Average of 28 alkali olivine basalts

Analysis 2 - Average of 37 olivine tholeiites

*(Data from Ellis and Ferguson, 1976)

In the upper reaches of the Loddon Valley, the newly recharged groundwaters in the Calivil Formation are of the calcium-sodium bicarbonate-chloride-sulphate hydrofacies. The waters reflecting the influence of the basalts are either saturated or near to saturation in magnesite, calcite, and dolomite (Figure 5.3); therefore, initially, on passing downbasin, the increased salinity is accompanied by relative rises in Na⁺, Cl⁻ and SO₄²⁻, while Ca²⁺, Mg²⁺ and HCO₃⁻ remain fairly constant. Using percentage as a basis, plots of anions and cations show an initial rapid falloff in

the latter ions, while the former show a commensurate rise (Figure 5.2). Thus, even a slight rise in salinity results in the development of a sodium-magnesium chloride-sulphate-bicarbonate hydrofacies while still well within the highland tract where chlorinity values are only slightly above 200 mg/l. This stage has already been reached at Moolort, and, on passing further downbasin, the trend continues until a chloride-sulphate hydrofacies develops in the northern Calivil district on the Loddon Plain. In the case of the cations, the $\text{Ca}^{2+} + \text{Mg}^{2+}$ percentage remains less than 50%, being about 20% to 30% over most of the section. Under Back's (1961) classification, this is a Na^+ - Ca^{2+} water; however, given the ascendancy of the Mg^{2+} ion over the Ca^{2+} , it can be better considered as a Na^+ - Mg^{2+} water, and this category is preferred in Table 5.1.

While, in the uppermost regions of the Loddon Valley, the cation ratios undergo rapid changes as the Na^+ percentage rises relative to Ca^{2+} and Mg^{2+} , this lasts for only a short distance on passing downbasin before leveling off. Indeed, perhaps the most striking feature of the groundwater chemistry is seen in the cation percentages (Figure 5.2), which show that by about chlorinities of 600 mg/l (about 1,400 mg/l, TDS), that is, in the vicinity of the Pompapiel district, the groundwaters have virtually reached an equilibrium situation, having constant cation ratios, which change only slightly on crossing the Loddon Plain. The concomitant rise in Ca^{2+} and Mg^{2+} to that of Na^+ , as salinity increases, occurs despite the saturation or near saturation of the groundwaters with respect to the carbonate phases. At the same time, there is a steady decline in the percentage HCO_3^- and CO_3^{2-} species (shown only as HCO_3^- in Table 5.2), suggesting the ongoing precipitation of the carbonate phase, or its nonsolution.

The uniform groundwater character from Pompapiel northward shows that cation ex-change has virtually no effect within the Calivil Formation beneath the Loddon Plain, partially reflecting the lithology and mineralogy of the Calivil Formation, which consists, in this region, of clean, coarse-grained quartz gravel and sand, with no lithic fragments other than quartz. (Only one nonquartz fragment was obtained from the Calivil Formation during the drilling program undertaken for this investigation.)

In contrast to the cation ratios, which show little change after chlorinities of 600 mg/l, the anions show a marked increase in chloride percentage on passing down the basin and a concomitant decrease in bicarbonate (Figure 5.2). Although initially somewhat irregular, there is a general trend for the sulphate to remain constant, within a range of 3-14% overall, and from 7-11% beyond Bridgewater. The rate of decline of the bicarbonate + carbonate percentage is rapid until chlorinities of about 1,300 mg/l are reached (approximately 2,700 mg/l, TDS), after which, although still continuing to decline, the rate of decline levels off.

Given the above trends, it can be shown that the chloride-cation ratios, although undergoing initial rapid rises (less in the case of chloride-sodium), become more constant by chlorinities of about 800 - 1,000 mg/l. This stabilization is reached in the Pompapiel to Calivil region on the Loddon Plain. Apart from rises in the Cl percentage and falls in the HCO_3^- percentage, the character of the groundwater is relatively uniform beyond Calivil, with only salinity showing any significant changes as it rapidly rises from 2,300 mg/l to over 6,000 mg/l in the parish of Mologa immediately to the north.

Perhaps the most significant aspect of the trends, in terms of the downbasin evolution of the groundwaters, is that by the time salinities have reached values of only about 2,000 mg/l the waters are already plotting close to the field of seawater (Figure 5.4a). Therefore, by this early stage, the groundwaters have already obtained a distinct oceanic character, which is only slightly modified on further concentration. The trend towards an oceanic character is also present in groundwaters contained in shoestring sand aquifers in the overlying Shepparton Formation of the southern Loddon Valley, and in waters of a Murray Valley lead system in the northernmost regions of the Loddon Plain (Figures 5.4b and 5.4c). While it could be argued that a connate seawater influence may have been present since the early Pliocene sea transgressed this far inland, it is not the case with the waters from the upper Loddon Valley, which come from a continental setting well beyond the limits of the Pliocene sea. Similar trends occur in the

groundwaters from the Campaspe Valley (Figure 5.5a).

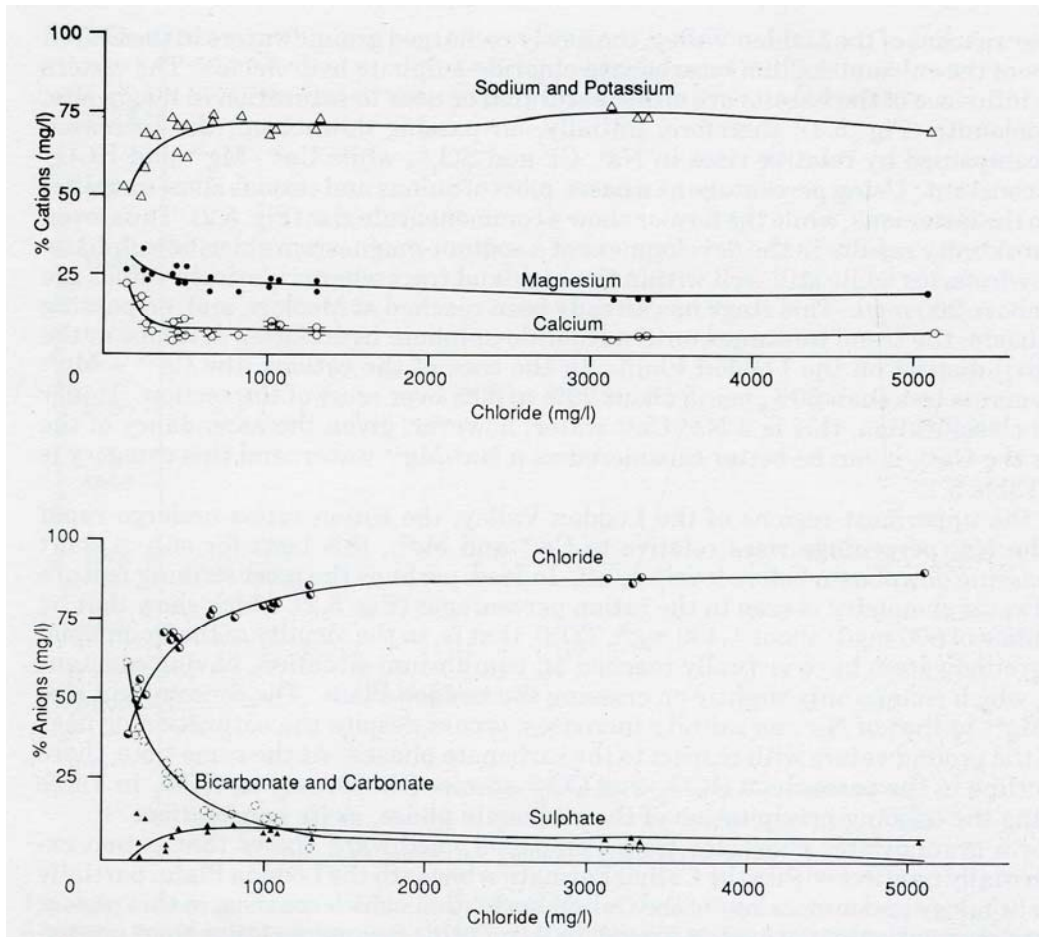


Figure 5.2 - Cation and anion percentages versus chloride concentration - Calivil Formation, Loddon Valley (between Moolort and Mincha West)

The early attainment of an oceanic character by the regional groundwaters while still well within a continental setting is an important consideration in any discussion of the origin of the saline oceanic-type groundwater in the marine Parilla Sand aquifer (Figure 5.5b), which is the downbasin continuation of the Calivil Formation aquifer in terms of regional groundwater flow (Chapter 4.2).

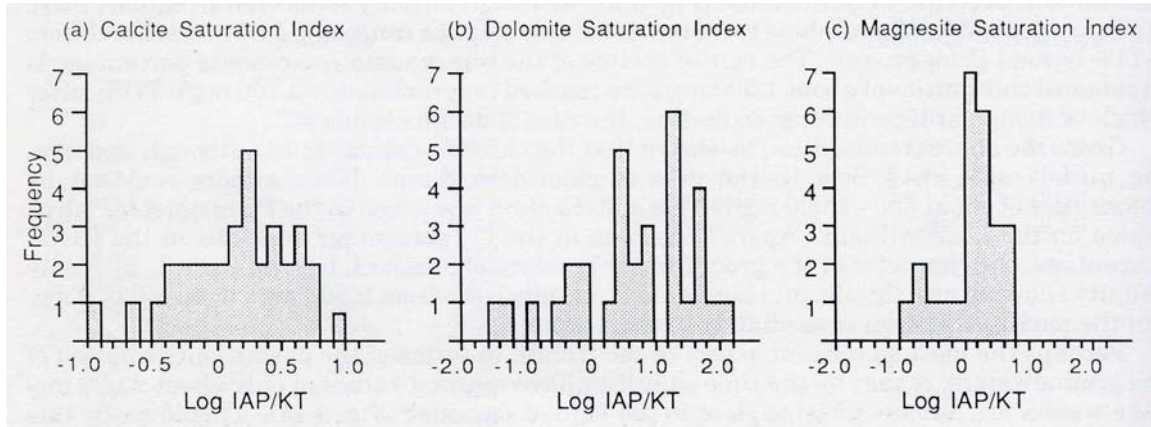


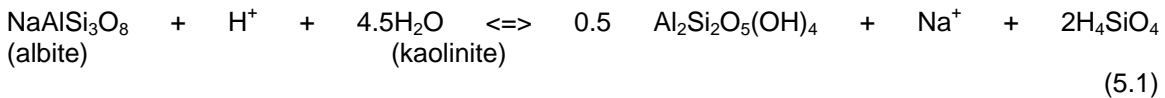
Figure 5.3 – Carbonate phase saturation indices – Calivil Formation, Loddon Valley

5.4 Silicate Equilibria in the Calivil Formation Aquifer

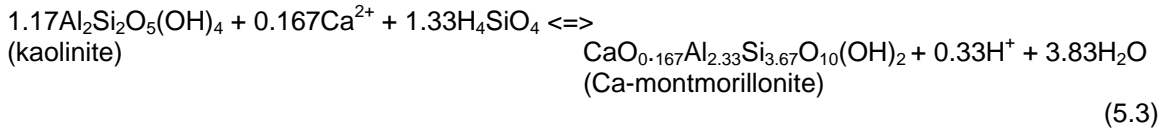
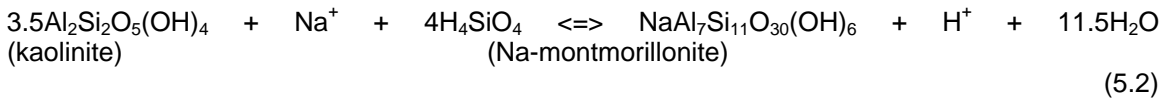
5.4.1 Evolutionary Trends in Silicate Equilibria

The early attainment of cation equilibrium along the flow path causes groundwaters which occur in the highland tract to be already essentially chemically mature: they undergo little further evolution on passing downbasin. A similar evolutionary trend towards chemical maturity in silicate equilibria was suggested by Helgeson et al., (1969). This process commences with the incongruent dissolution of aluminosilicate minerals by CO₂ enriched groundwaters, which convert feldspars and micas to kaolin, with a corresponding increase in Na⁺, Ca²⁺, K⁺, Mg²⁺, and H₄SiO₄ relative to H⁺ (Stumm and Morgan, 1970).

For example:



Following further weathering and the increased availability of silica and cations, the kaolinite can then be converted into montmorillonite as follows



The implication is that the sediment-water system is closed, and, therefore, there is no loss of ions from the system. However, in natural systems, when feldspar-rich igneous rocks are infiltrated by aggressive recharge waters rich in CO₂, they are leached of cations and silica. While the initial response is to form gibbsite, the amount of silica cations released is normally more than sufficient to convert the gibbsite to kaolinite (Stumm and Morgan, 1970). As the process proceeds, the cation and silica concentrations steadily increase to a point where the kaolinite starts converting into montmorillonite. Predominance diagrams illustrating the typical progress of mineral stability in the weathering process are shown in Figure 5.6 (from Stumm and Morgan, 1981).

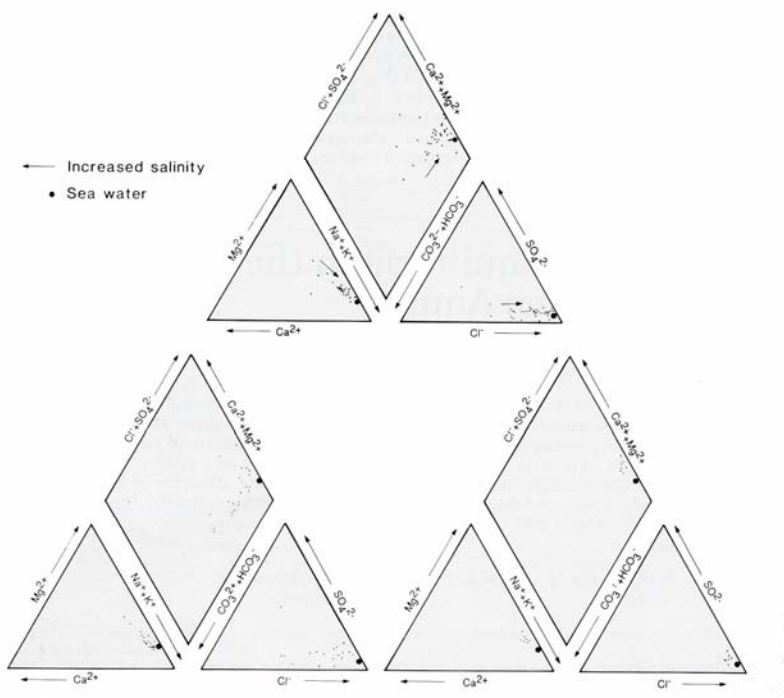


Figure 5.4a - Hydro-chemistry of the Calivil Formation - Loddon Basin

Figure 5.4b - Hydro-chemistry of the Shepparton Formation on the southern Loddon Plain

Figure 5.4c - Hydro-chemistry of Calivil Formation - Murray Valley lead on the northern Loddon Plain

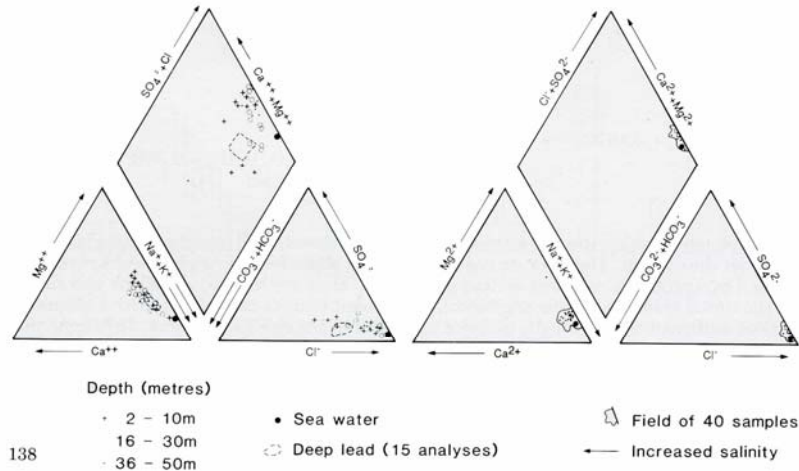


Figure 5.5a - Hydro-chemistry of Campaspe Valley groundwaters (from Tickell, Unpub.)

Figure 5.5b - Hydro-chemistry of Parilla Sand

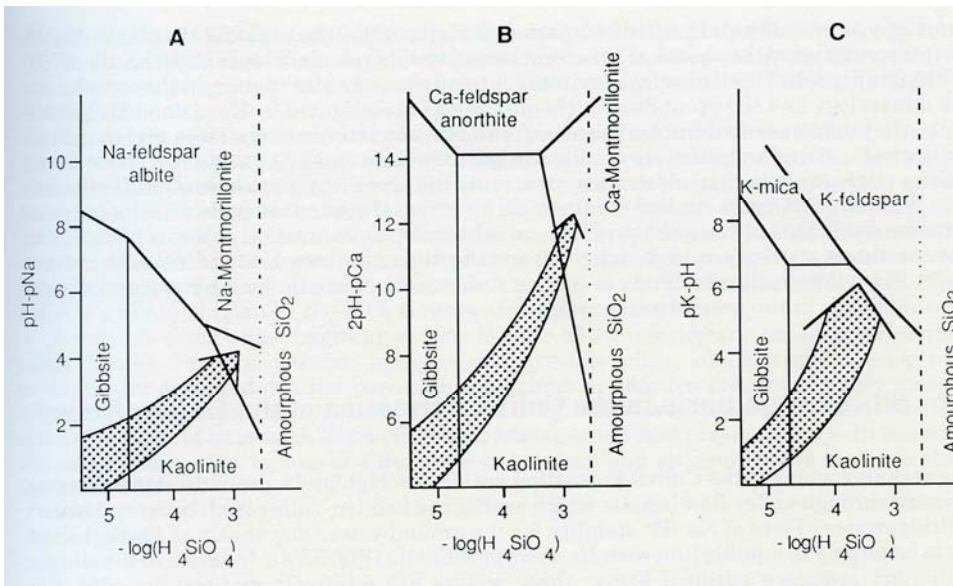


Figure 5.6 - Predominance diagrams illustrating the stability relationships between gibbsite, kaolinite, montmorillonite and feldspars. Arrows indicate hypothetical paths taken during the weathering process (after Stumm and Morgan, 1981).

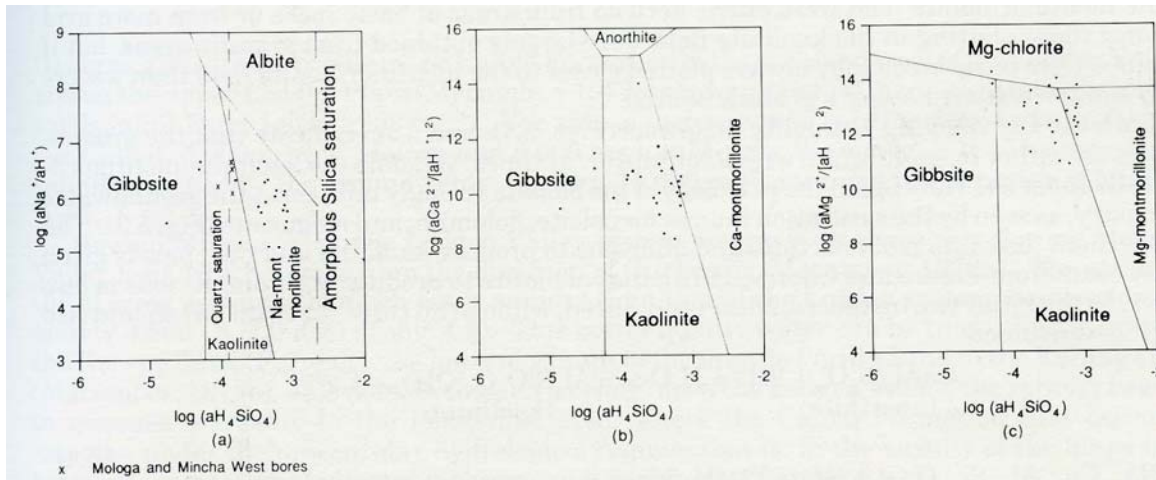


Figure 5.7 - Silicate stability diagram, Calivil Formation, Loddon Valley (at 25° and 1 bar)

Groundwaters in equilibrium with the solid phase minerals will show similar characteristics, which maybe demonstrated by means of activity diagrams (Garrells and Christ, 1965). The boundaries between the differing mineral phases are based on thermodynamic data; however, the constants used may vary between individuals, which in turn leads to differences in the position of the boundaries. The stability boundaries chosen for use in this study are taken from the work of Nesbitt (1977). Slightly different boundaries are shown in Figure 5.6 from Stumm and Morgan (1981), while Tardy (1971) has a further set of boundaries. The stability boundaries are based on pure minerals and, therefore, do not accurately represent the real systems in nature. Nevertheless, the equilibrium data provides a useful insight into the interactions of groundwaters with feldspars and clays, while the stability diagrams enable some interpretation of the chemical data from hydrological systems (Freeze and Cherry, 1979).

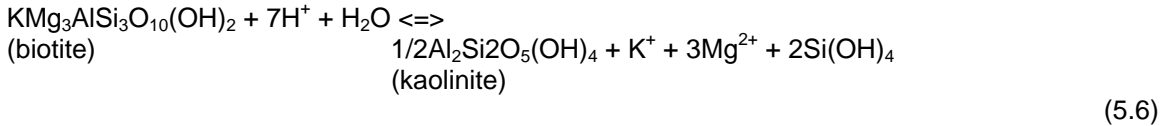
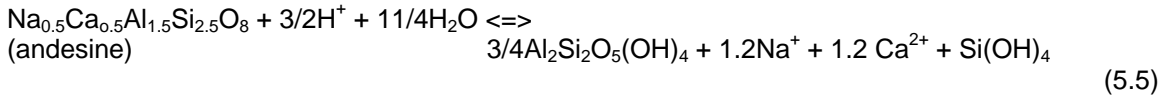
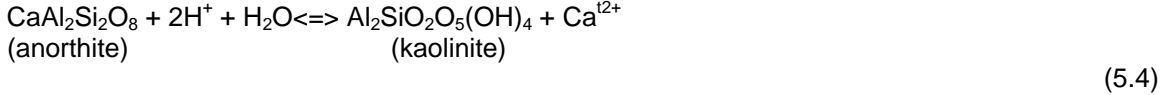
The significance of both physical environment and groundwater regime on the coevolution of the mineralogy and the groundwater chemistry was investigated by Kovda and Samoiloova (1969). They demonstrated the preferential formation of kaolinite in the more humid upland regions where cations and silica are readily flushed from the weathering sequence. The cations and silica migrate via the groundwater systems into the lower regions, where montmorillonite forms. Wallick (1981), who studied the chemical evolution of groundwaters in a drainage basin in Canada, noted that in the more arid regions, where the concentration of Na^+ is high (due to the precipitation of calcite, cation exchange, and the higher ionic mobility of Na^+ with respect to Ca^{2+}), Na-montmorillonite tends to be the stable solid phase in lowland areas and with increasing depth in the groundwater system.

5.4.2 Silicate Equilibria in the Calivil Formation of the Loddon Valley

In the recharge zones of the Calivil Formation within the highlands, groundwater infiltrates downward through valley flow basalts which overlie the Loddon Valley lead, between Moolort and Bridgewater. Plots of Na^+/H^+ stability for the groundwaters downbasin of Moolort show them to be largely in equilibrium with Na-montmorillonite (Figure 5.7a). In terms of the silicate evolutionary sequence outlined above, these waters are relatively mature; however, this apparent maturity probably arises directly from influence of the basaltic recharge areas. The groundwaters are oversaturated with quartz, which was probably derived from the aluminosilicates in the recharge areas. It was shown by Tardy (1971), who sampled 450 waters from a number of countries having differing geological and climatic regimes, that waters which plot in the montmorillonite field were either derived from areas of basic rocks or from more arid regions; those plotting in the kaolinite field were largely obtained from granitic areas, but if obtained from basic areas they always plotted closer to the montmorillonite field than waters from similar regions having a

granitic source.

Both the Ca^{2+} and Mg^{2+} stability diagrams (Figures 5.7b and 5.7c) indicate that the groundwaters are either in equilibrium with kaolinite or, at times, straddle the kaolinite-montmorillonite boundaries. Here again the petrology of the basalts strongly influences the groundwater chemistry, as seen by the saturation indices for calcite, dolomite, and magnesite (Figure 5.3). The incongruent dissolution of anorthite and andesine to produce kaolinite and Ca^{2+} ions is given below (data from Freeze and Cherry, 1979); that of biotite to produce Mg^{2+} and K^+ ions is also given. In the latter two instances, silica is produced, while in all three cases the pH should rise as H^+ is consumed.



While the silicate stability diagram indicates that the groundwaters are in equilibrium with Na-montmorillonite in the recharge areas of the highlands and the upper parts of the plains, in the lower regions of the flow path, where the Calivil Formation trench is incised into deeply weathered (kaolinized) Palaeozoic sediments, the chemical equilibrium swings toward the kaolinite field (Figure 5.6a). An indication of this trend can be seen in the silica content of the groundwaters, which falls away sharply in the northern parishes of Mologa and Mincha West (Table 5.2).

It can be seen therefore, that despite the general evolution of the Calivil Formation groundwaters toward uniformity and maturity, even at an early stage along the flow path the trends within the silicate stability do not show any comparable pattern but appear to relate more to the mineralogy of the area through which they are passing. While the presence of high SiO_2 and Na^+ content is essential to the development of groundwaters in equilibrium with Na-montmorillonite in the upper and central regions of the flow path, the movement of the equilibrium toward kaolinite in the lowermost regions is not due to a lack of Na^+ but instead reflects a diminishment in the SiO_2 content of the groundwaters.

A possible error which might arise from the use of the colorimetric analysis technique for silica derives from the possible presence of polymeric silica, which might develop in the groundwater system down the flow path with time; in addition colorimetry only measures silica above the dimer (R.J. McLaughlin, pers. com.). However, should polymerization have occurred, it would have been followed by aggradation and rapid precipitation with essentially the same result, that is, loss of silica from the system and an equilibrium closer to that of kaolinite.

5.5 Salinity Profile down the Loddon Valley

General: The salinity profile in the Calivil Formation in the highland tract of the Loddon Valley and on the upper Loddon Plain (Macumber, 1978c) shows a gradual increase in total dissolved solids, until Pompapiel (1,250 mg/l). The rate of increase then rapidly rises, to be 2,200 mg/l at Calivil, 6,000 mg/l at Mologa and 9,000 mg/l at Mincha West (Figure 5.1). The maximum salinity reached by the groundwaters is about 15,000 mg/l, recorded in the parish of Mincha West.

Beyond Mincha West, the Loddon Valley system merges with a westerly flowing Murray Valley lead, which passes from the direction of Gunbower (Macumber, 1978a). The water in the Murray system is of much lower salinity than that of the Loddon system, being approximately 3,500 - 6,500 mg/l (Table 4.2). This better quality water can be traced westward into the Kerang Sand (Figure 4.6c), the lowermost unit of the marine Parilla Sand in the Kerang area (Macumber, 1978b). It is notable that, on passing down the Loddon Valley, the salinity begins to increase markedly in the Pompapiel area, where the Calivil Formation first becomes artesian under the present-day hydrological regime, that is, in the vicinity of the hinge line between regional groundwater recharge and discharge (Chapter 4.1.11).

5.6 Factors which Influence Groundwater Salinity

Mechanisms which control the chemistry of groundwaters are well known, and those which influence the Murray Basin groundwater systems have been previously listed by Lawrence (1975). Certain of these processes have been referred to in more detail in the discussion above, while others are described elsewhere in this report. A brief resume of these processes is given below:

- i. The addition of atmospheric salts, which fall with rainwater.
- ii. Addition of carbonates, formed by the solution of CO₂ which is produced in the soil zone by the decay of organic matter and the respiration of microorganisms.
- iii. The addition of oceanic connate water. (This does not appear in the fluvial sequences, away from marine sequences.)
- iv. Dissolution of evaporite minerals such as gypsum, calcite and halite.
- v. Oxidation of pyrite to give sulphate, and the reduction of sulphate to sulphide, in the presence of sulphate-reducing bacteria.
- vi. Cation exchange on clays.
- vii. Ultrafiltration, or salt sieving, by semipermeable clay membranes.
- viii. Chemical weathering of silicate minerals (as discussed above).
- ix. Concentration by evaporation or evapotranspiration.
- x. Residence time. It follows that a longer residence time permits the above listed processes to proceed further, thus increasing salinities.

Undoubtedly, many of these processes contribute toward the chemical character of Calivil Formation waters at some stage along their evolutionary tracts and are responsible for the trends described by Chebotarev (1955), whereby groundwaters tend toward a seawater composition while at the same time steadily increasing in salinity. However, in the case of the Calivil Formation waters of the Loddon Valley, the rapid salinity increase occurs well after chemical equilibrium has been reached and after many of these processes (for example, cation exchange) have virtually ceased to be active. Of the processes listed, most may be discounted as contributing to the salinity increase, leaving only two or three for which discussion is warranted, and these are considered below.

5.6.1 Residence Time

It is generally believed that groundwater salinity may simply reflect residence time in the aquifer, that is, sluggish waters and long flow paths lead to higher salinities. The main basis for this opinion is that the above listed processes have continued to be active over a considerable time and for a significant part of the flow path. The effects of residence time are thus reflected by the evolutionary trends of the groundwater chemistry as well as by the gross salinity increases. Yet, this broad generalization does not explain the sudden salinity increase in the aquifer well after chemical equilibrium has already been attained. Indeed, along its entire length the clean channel-fill quartz gravel of the aquifer maintains a moderately high hydraulic conductivity, ranging from 85 m/d at Bridgewater where the salinities are only 1,200 mg/l, to 43 m/d at Mincha West where the salinities are over 9,000 mg/l. Therefore, despite a gradual decrease in hydraulic conductivity, the flow system maintains a fairly high velocity throughout, giving a calculated flow time from Bridgewater to Mincha West of less than 3,000 years (the hydraulic gradient over this interval being about 0.6 m/km). Individual flow velocities at Bridgewater, Calivil, and Mincha West are given in Table 5.4. These values are calculated from the Theis equation, using a porosity value of 0.4, the maximum likely value. For porosities of 0.2, perhaps a better average porosity, the velocities would double and the residence time halve. The hydraulic conductivity values are from

Table 4.1, Chapter 4.2.

TABLE 5.4 - Aquifer parameters and flow velocities - Calivil Formation of the Loddon Plain

Station	Hydraulic Conductivity (m/d)	Hydraulic Gradient ($\times 10^{-3}$)	Velocity (m/year)
Bridgewater	85	0.86	67
Calivil	49	0.55	25
Mincha West	43	0.38	15

5.6.2 Ultrafiltration

The concentration of groundwater by a process of pressure-induced filtration through semipermeable clay membranes (ultrafiltration) has been reviewed by White (1965) and Berry (1969). The process is discussed in some detail in Chapter 12.16.2.

Because the initial increase in the rate of rise of salinities occurs in the part of the aquifer where the groundwater system is either artesian or lies in an artesian transition zone, and the highest rate of salinity increase occurs in the Calivil-Mincha West region, where the overlying aquitard is predominantly clay (and at its most effective), then further consideration must be given to ultrafiltration as a process which might explain the salinity pattern observed in the Calivil Formation aquifer.

Based on observations of downaquifer groundwater salinity increases in three areas (the mid-Continental area, the Woodbine Sandstone of Texas, and the Illinois Basin), Bredehoeft et al. (1963) constructed a model to explain the rapid salinity buildup in aquifers which discharge into closed basins. They put forward a process whereby under artesian conditions, water passing down an aquifer system may discharge upward through an argillaceous aquitard, which acts as a semipermeable membrane permitting the passage of formation waters but retarding the transfer of dissolved ions. The ions are thus retained in the aquifer and cause a salinity build up. The degree of ionic concentration in the aquifer is dependent on the efficiency of the clay membrane overlying the aquifer. Bredehoeft et al. give a series of graphical solutions to the downbasin salinity increases for varying membrane efficiencies, based on the formula

(5.7)

- C_w = concentration at distance w from centre of basin
- C_i = concentration of recharging waters
- r = the radius of the basin
- w = distance of point at which concentration is sought
- (1-e) = membrane efficiency

It would seem not possible to apply the formula directly to the Loddon Valley, since the aquifer system although wedging to the north is open-ended at its downstream end. However, as stated by Bredehoeft et al., an almost infinite variety of geological considerations violates the mathematical model. The Loddon Valley as a hydrological basin departs from the model at both its upstream and downstream ends. In the former instance, the system is overlain by, at best, an aquitard, while, in the latter case the basin is not closed but instead only wedges to the north before becoming tributary to the Murray system.

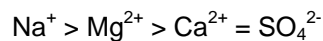
Nevertheless, given these limitations, there is a surprising degree of agreement in salinity values obtained from the Theoretical Concentration Linear Head Model, where,

and those occurring along the Loddon Valley between Bridgewater and Mincha West. Here, the basin radius is taken as being 198 km (passing from Ballarat on the divide due north to the Murray River). The initial concentration (C_i) used for the calculations is 500 mg/l, a figure that approximates the average salinity in the headwater catchment areas. The membrane efficiency is taken as 1. However, where clay membrane sieving occurs it should be accompanied by selective ion filtration.

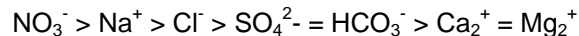
5.6.3 Selective Ion Filtration

A membrane sieving hypothesis was adopted by White (1965) to explain the chemistry of certain North American saline groundwaters. Examples of membrane filtered and membrane concentrated connate waters are given by White, and the rates of migration and the degree of chemical change are considered by him to be dependent on the attendant physical and chemical environments. The initial driving force is seen by White as being lithostatic pressure, after which meteoric waters provide the driving energy under certain circumstances of topography, structure and lithology. Lithostatic pressure is, however, not relevant to the Calivil Formation aquifer, since the situation in the Loddon Valley is not one arising from the compaction of fine-grained sediments containing connate water but, instead, derives from hydraulic heads on meteoric waters. White states that the relative ion mobilities are, in part, consistent with the hypothesis that small single-charge ions are the most mobile and large double-charged ions the least mobile. There is, however, an admission by White that further work is needed in order to fortify or revise the tentative conclusions.

White proposed the order of ion mobility as



Experimental work by Larson (1967) using cellulose acetate membranes suggested that the mobility order was



Unlike the case with the Bredehoeft et al. model, it is difficult to fit the chemical evolution of the groundwater on its passage down the Loddon Valley into the pattern obtained by White. In order to agree with White's hypothesis, decreased Na/Ca, Na/Mg, Na/SO₄, Cl/Ca, Cl/Mg and Cl/SO₄ ratios should occur. But this is not so, since the cation ratios remain roughly constant throughout the system (Figure 5.2). Of the anions, it is the Cl⁻ that shows a tendency to increase preferentially relative to other ions. Like the cations, SO₄²⁻ remains fairly constant, while the HCO₃⁻ shows a marked decrease. An explanation of the latter trend could be contained in White's comment that CO₃²⁻ can migrate across the clay membrane as either uncharged H₂CO₃ or as undissociated NaHCO₃⁻. An order of mobilities, based on the downbasin trends in the Calivil Formation aquifer would be Cl⁻, low; Na⁺, Mg²⁺, SO₄²⁻, Ca²⁺, intermediate; and HCO₃⁻ high.

Therefore, while using only total dissolved solids, a reasonable fit may be had with the mathematical model; however, the hydrochemical data indicates that salt sieving is not a significant process in the salinity increase in the Calivil Formation waters.

5.6.4 Non-Steady State Flow - Salinity Increase in the Discharge Zone

Under the present-day hydrological regime, the Loddon Plain, from Pompapiel in the south through to the Murray River in the north, is underlain by an aquifer which is either artesian or close to being artesian. Between Bridgewater and Mincha West, a distance of about 80 km, there is a loss of over 90% of the water from the Calivil Formation aquifer, partly into the Renmark Group and partly into the overlying Shepparton Formation (Chapter 4.1.11). Over parts of the plain, groundwater discharge to the surface is observed, and elsewhere it is inferred. While some of the outflow occurs as base flow into stream systems and as spring outseepages such as at Bears Lagoon, much of the outflow is deemed to be lost by evapotranspiration and evaporation

from the soil water zone.

While, prior to European settlement artesian conditions would have occurred within the Calivil formation on the Loddon Plain, they were probably not as extensive as they are today. Once irrigation commenced, however, topping up of the excess aquifer storage would have led to a rapid lateral expansion of the regional groundwater discharge zone with the upbasin extension of these conditions. Over much of the Loddon Plain, water tables are now within 1-2 m of the surface, resulting in an epipercolative water regime (cf. Yaalon, 1963), whereby salt accumulates within the soil zone or at the surface (Figure 5.8). About one-third of the area in the mid-Loddon Valley has a high or very high soil salinity. The salinity of the shallow groundwaters is correspondingly high, with salinities ranging from about 10,000 up to 60,000 mg/l. A palaeohydrological regime similar to that existing today was previously documented as occurring at Kow Swamp at the northernmost limits of the Loddon Plain in the early Holocene Period, when high water tables resulted in the loss of trees from the plain (Macumber, 1977).

Indeed, cycles of salinization are seen as recurring events on the Loddon Plain throughout the Quaternary Period whenever high water budgets existed on the plain (Macumber, 1968). The rapid response of the Calivil Formation aquifer in 1973-75 to only several wet years indicates that a very delicately balanced hydrological equilibrium exists in the groundwater system. It also shows that over a period of time, for example, spanning the latter half of the Holocene Period, the aquifer would have responded to any extended wetter or drier events by advances and retreats in the recharge-discharge hinge line. It is plausible to envisage a broad zone in the upper to central Loddon Plain, where the flow system may at one time have a vertical flow component downward, and at another time upward, as was the situation in the Pompapiel area over the period 1970 to 1980. That is, non-steady state conditions exist in the aquifer.

In response to temporary climatic fluctuations, there is an episodic pressure fluctuation developed in the regional groundwater flow system during which, under high hydraulic head, water migrates from the aquifer to the surface where it either evaporates or evapotranspires, and allows high salt concentrations to build up in both the soils and the shallow groundwaters. Under lower aquifer pressures, downward directed vertical hydraulic gradients permit the leaching of salts from the vadose zone into the regional subsurface drain - the lead. It is therefore suggested that there is an influx of salts superimposed upon the regional flow system along its length, starting from a point in the vicinity of the upstream limits of the recharge-discharge hinge line, whenever lower hydraulic head conditions prevail in the aquifer and the discharge zone shrinks.

While much of the salt entering the groundwater system during times of lower aquifer pressures could have come initially from the Calivil Formation aquifer, it is likely that part of the recharging salt was deposited on the plain by the stream systems during phases of sheet flooding (cf. Macumber, 1969). A process of episodic salt infusions would explain the observation that the initial increase in the rate of rise of groundwater salinity commences in the Pompapiel district, that is, in the vicinity of the present-day hinge line.

Since the addition of salts from this source only commences downbasin of the former hinge line, then the most northerly waters, having spent the longest times in the zone of periodic salt accretion, will be the most saline, and, to this extent, residence time is relevant to salinity increase. The rate of salinity increase with distance downbasin will then depend upon such factors as the downbasin flow velocity and the period for which the low-pressure conditions prevail. Of the factors previously listed, the non-steady state flow model of salinity increase best fits into the evaporation-evapotranspiration category, with the rider that the evaporative process takes place at some distance above the aquifer, at or very close to the surface.

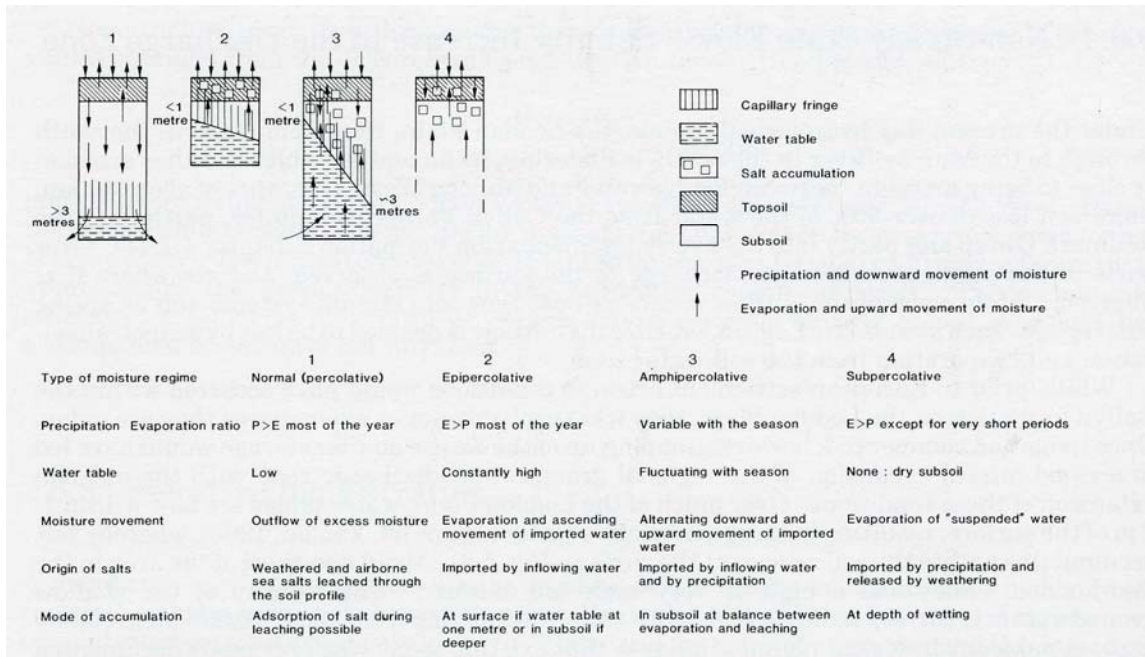


Figure 5.8 - Schematic diagram of characteristic soil moisture regimes, showing their relation to salt accumulation (after Yaalon, 1963).