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The Use of Environmental Chloride and Tritium to Estimate Total Recharge to an Unconfined Aquifer

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Abstract

A portion of the Gambier Plain underlain by an unconfined aquifer with readily definable hydrologic boundaries has been divided into a number of areas within which soil types have similar hydrologic properties. Mean annual recharge has been estimated for each area using both the tritium concentration and the chloride concentration of water within the soil profile. Good agreement was obtained between the two methods with local recharge varying between 50 and 250 mm year^{-1}.

Total mean annual recharge for the area has been estimated to be $2 \cdot 4 \pm 0 \cdot 3 \times 10^8$ m^3 year^{-1}, and this compares favourably with an estimated discharge of $2 \cdot 5 \pm 0 \cdot 3 \times 10^8$ m^3 year^{-1}.

Introduction

Several workers (for example, Smith *et al.* 1970; Allison and Hughes 1974; Anderson and Sevel 1974) have shown the usefulness of measurements of natural tritium in the unsaturated zone of the soil for evaluation of local recharge. Most of the interpretation has been on the basis that water in the soil profile beneath the root zone moves by piston flow. A knowledge of the history of the variation of the tritium concentration (TC) of precipitation, together with the variation of TC of soil water with depth, enables estimation of local recharge to be made.

Chloride is another tracer which, in principle, can be used to estimate local recharge. Like tritium, it is input at the soil surface in precipitation, but unlike tritium, it is concentrated by evapotranspiration, the amount of this concentration being determined by the ratio of recharge to precipitation. Surprisingly little use of chloride as a tracer for estimating recharge has been made. Anderson (1945) discussed recharge and run-off over a large portion of southern Australia, but his study was hampered by lack of suitable data for the input of chloride. Eriksson and Khunakasem (1969) studied recharge to the Coastal Plain aquifer of Israel using the chloride concentration of groundwater. They needed to assume that if chloride concentrations of water were obtained at a large number of different locations and depths, the isohalsines constructed using these data represented averages over the whole depth of the aquifer.

One of the difficulties in a study of this type is that the ratio of annual recharge to total volume of the aquifer is often small, and since recharge is usually dependent on land use, the land use pattern needs to have remained unchanged for a considerable length of time for a steady state to be assumed. For example, Peck and Hurle (1973) studied the chloride balance of a range of Western Australian catchments undergoing changes in land use. They found chloride concentrations in groundwater from cleared but once forested catchments many times higher than the predicted value for the new land use. In their rather small catchments ($0 \cdot 4$–380×10^3 ha), the time estimated for chloride equilibrium to be re-established after clearing ranged from 20 to 400 years.

The aim of this present work is to use soil water tritium and chloride concentrations to estimate the total mean annual recharge to the Gambier Plain unconfined aquifer. This local recharge is an important parameter in planning future development of the area. In an earlier paper (Allison 1975) a preliminary attempt to estimate total annual recharge using natural tritium was described. This paper reports the extension of the network of observation sites and a comparison of estimates of recharge using natural tritium and chloride.

The Study Area

Geography

The area (Fig. 1) and land use have been described previously (Blackburn 1959; Allison 1975). Mean annual rainfall varies between 700 and 750 mm year^{-1}, most of which falls in the winter. There is almost no surface run-off, and drainage occurs through the soil to an underlying Oligocene–Miocene limestone aquifer (the Gambier Limestone), which in some localities was reworked during the Pleistocene. A confined Eocene sand aquifer (part of the Knight Group) underlies the limestone. The two aquifers are considered to be separated over most of the study area by an aquitard of varying thickness which prevents substantial leakage from the unconfined aquifer. Obvious discharge from the upper aquifer occurs via spring flow near the coast.

All terrestrial boundaries in Fig. 1 are streamlines identified from a network of bores on a $1 \cdot 6$ km grid over most of the study area (Waterhouse 1975). The area of this groundwater catchment is 1620 km^2, compared with 1440 km^2 used in the previous paper. This difference is due to the fact that more bore hole data are now available, enabling better definition of streamlines to be made.

Soils and Land Use

Data reported in an earlier study (Allison and Hughes 1974) showed that local recharge is dependent on soil type. The soils of the study area range from the rather impermeable swampy podzols which can develop high soil moisture deficits, to the very permeable, skeletal soils of low water-holding capacity which are usually only 50–200 mm thick and found developed directly on top of the highly permeable Gambier Limestone.

The area was partitioned into 10 different hydrologic units as shown in Fig. 1. The soils within each hydrologic unit are considered to have similar hydrologic properties, and hence similar mean annual recharge (MAR). Boundaries were drawn in consultation with Mr G. Blackburn, a pedologist with considerable experience in the area, and using the Geological Map of Gambier and Northumberland (1 in. to 1 mile, Geological Survey of S.A. 1951), together with a detailed soil map of the area (Blackburn 1959).

Some irrigation is practised, but the area of land irrigated is only approximately 2% of the total (Aust. Bur. of Statistics, private communication 1976). Approximately 15% of the total area is planted to *Pinus radiata*. Earlier work has shown that local recharge beneath these forests is much less than that beneath the surrounding grassland (Holmes and Colville 1970; Colville and Holmes 1972; Allison and Hughes 1972). For the purposes of the present work it is assumed that no local recharge occurs beneath the forests. The coastal swamps (3% of the total area) are identified as groundwater discharge areas and therefore also have no net local recharge.

Sampling Sites

Sixteen sampling sites (Fig. 1) were chosen to give a representative cover of the different hydrologic units. All sites were on improved pasture which is the dominant land use of the area.

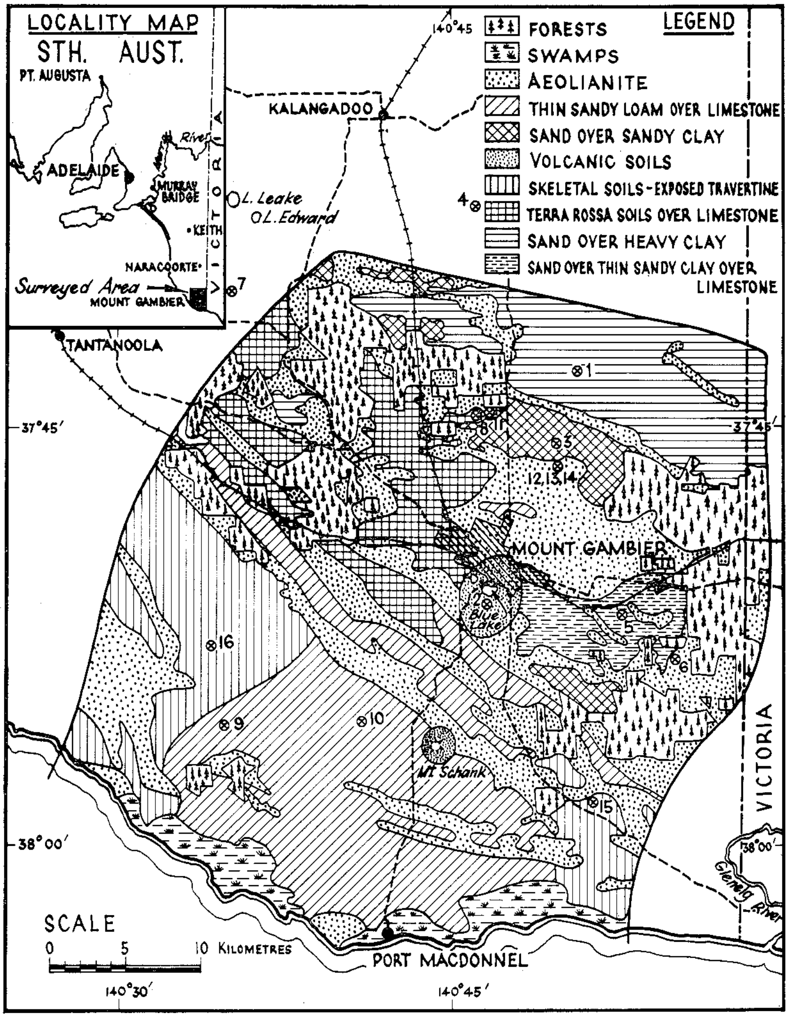

Fig. 1. The study area showing the hydrologic units.

Techniques

Soil cores of 100 mm diameter were collected from depths to 10 m at each site. They were cut into 300 mm sections, stored and treated as previously described (Allison and Hughes 1974). Subsamples of each section were taken for chloride analyses. Water samples only were taken beneath the water table.

Table 1. The variation of tritium concentration, chloride concentration and water content with depth at each site

Notes: Values in table are mean values for each depth interval. Tritium concentration and water content for sites 1, 4 and 7 reported previously (Allison and Hughes 1974). Tritium concentration and water content for site 10 reported previously (Allison 1975)

	Site no. 1	Site no. 2			Site no. 3			Site no. 5			Site no. 6		
Depth (m)	Chloride (mg l^{-1})	Chloride (mg l^{-1})	TC (TU)[B]	Water content (cm^3/cm^3)	Chloride (mg l^{-1})	TC (TU)	Water content (cm^3/cm^3)	Chloride (mg l^{-1})	TC (TU)	Water content (cm^3/cm^3)	Chloride (mg l^{-1})	TC (TU)	Water content (cm^3/cm^3)
0 –0·5	122	44	14·8	0·20	390	12·8	0·16	108	14·8	0·23	24	16·4	0·25
0·5–1·0	131	175	9·6	0·15	340	14·8	0·07	111	13·8	0·25	47	23·6	0·16
1·0–1·5	76	250	17·0	0·13	82	14·6	0·25	70	14·4	0·32	55	21·6	0·10
1·5–2·0	189	200	17·0	0·12	82	14·2	0·26	55	14·0	0·30	48	17·2	0·10
2·0–2·5	138	155	18·2	0·15	79	12·0	0·31	70	13·2	0·16	49	13·8	0·09
2·5–3·0	327	110	17·0	0·21	82	9·0	0·35	69	15·4	0·12	74	17·4	0·08
3·0–3·5	365	95	16·0	0·22	123	8·2	0·39	65	16·8	0·11	76	17·4	0·09
3·5–4·0	250	62	16·0	0·25	106	5·4	0·46	65	16·9	0·11	53	14·2	0·10
4·0–4·5	195	62	16·6	0·28	80	12·0	0·67	69	15·6	0·12	45	10·0	0·11
4·5–5·0	144	50	16·8	0·28	77	13·0	0·54	65	14·0	0·13			
5·0–5·5	97[A]	58	16·8	0·26	108	11·6	0·51	64	14·0	0·14			
5·5–6·0	70				130[A]	11·2	0·50	66	15·2	0·14			
6·0–6·5	52							60	17·0	0·14			
6·5–7·0								58	18·6	0·14			
7·0–7·5								59	19·8	0·13			

[A] Signifies position of water table at time of sampling. [B] Tritium units.

Table 1 (*Continued*)

Depth (m)	Site no. 8 Chloride (mg l^{-1})	Site no. 8 TC (TU)	Site no. 8 Water content (cm³/cm³)	Site no. 9 Chloride (mg l^{-1})	Site no. 9 TC (TU)	Site no. 9 Water content (cm³/cm³)	Site no. 11 Chloride (mg l^{-1})	Site no. 11 TC (TU)	Site no. 11 Water content (cm³/cm³)	Site no. 12 Chloride (mg l^{-1})	Site no. 12 TC (TU)	Site no. 12 Water content (cm³/cm³)
0–0·5	10	11·4	0·16	134	13·2	0·30	85	24·9	0·11	20	15·7	0·14
0·5–1·0	30	12·3	0·17	62	13·6	0·25	105	14·2	0·06	24	15·7	0·10
1·0–1·5	45	12·2	0·18	86	15·2	0·15	102	13·0	0·07	28	17·6	0·08
1·5–2·0	50	15·6	0·20	91	18·7	0·17	65	20·6	0·07	19	20·8	0·09
2·0–2·5	47	13·4	0·21	85	19·7	0·17	28	23·6	0·17	27	20·8	0·10
2·5–3·0	28	13·8	0·40	150	20·2	0·17	27	21·8	0·34	35	20·6	0·11
3·0–3·5	35	14·6	0·54	195	20·8	0·20	25	19·8	0·45	35	25·0	0·12
3·5–4·0	44	16·2	0·28	175	20·0	0·21	23	17·8	0·50	26	20·0	0·13
4·0–4·5	52	16·3	0·13	197	18·0	0·20	28	16·0	0·47	20	17·4	0·15
4·5–5·0	60	15·0	0·37	129	18·4	0·20	29	15·2	0·43	18	18·0	0·15
5·0–5·5	67	12·8	0·14	100	19·2	0·24	35	15·5	0·43	17	19·2	0·15
5·5–6·0	62	14·4	0·19	85	20·2	0·34	38	11·9	0·37	17	19·7	0·16
6·0–6·5	57	16·9	0·09	80	20·0	0·38	45	8·0	0·23	18	19·7	0·23
6·5–7·0				75^{A}	19·8	0·44	39	6·4	0·17	20	18·8	0·28
7·0–7·5				74	18·3	0·44	39	5·6	0·23	20	17·0	0·24
7·5–8·0				74	16·8	0·44	45	4·9	0·38	18	16·0	0·32
8·0–8·5				73	14·7	0·44	35	5·0	0·47	22	15·1	0·36
8·5–9·0				72	12·8	0·44	40	5·8	0·51	26	14·2	0·33
9·0–9·5				72	10·8	0·44	45	7·5	0·53	25	13·0	0·28
9·5–10·0				71	8·8	0·44	38	10·4	0·60	25	13·0	0·20
10·0–11·0				71	6·0	0·44				26^{A}	15·5	0·15
11·0–12·0										22	16·5	0·23
12·0–13·0											15·8	0·40
13·0–14·0										25	13·8	0·50
14·0–15·0											12·6	0·50
15·0–16·0											10·2	0·50
16·0–17·0										44	8·0	0·50

^{A} Signifies position of water table at time of sampling.

Table 1 (*Continued*)

Depth (m)	Site no. 13 Chloride (mg l^{-1})	TC (TU)	Water content (cm^3/cm^3)	Site no. 14 Chloride (mg l^{-1})	TC (TU)	Water content (cm^3/cm^3)	Site no. 15 Chloride (mg l^{-1})	TC (TU)	Water content (cm^3/cm^3)	Site no. 16 Chloride (mg l^{-1})	TC (TU)	Water content (cm^3/cm^3)
0–0·5	13	15·8	0·15	14	18·8	0·17	105	15·2	0·13	80	19·5	0·20
0·5–1·0	10	16·7	0·14	7	17·0	0·18	141	12·0	0·10	55	15·2	0·18
1·0–1·5	13	17·0	0·13	37	16·8	0·33	128	11·6	0·08	40	10·2	0·16
1·5–2·0	17	16·7	0·15	23	15·4	0·54	90	13·6	0·12	22	9·8	0·18
2·0–2·5	13	16·0	0·17	23^{A}	12·6	0·63	103	14·6	0·12	64	10·8	0·15
2·5–3·0	18	15·0	0·18	21	13·2	0·68	110	13·6	0·08	55	14·4	0·17
3·0–3·5	27	14·3	0·17	18	14·6	0·60	97	14·8	0·10	55	15·6	0·20
3·5–4·0	32	14·3	0·32	16	12·8	0·57	78	17·2	0·12	69	14·6	0·21
4·0–4·5	30	15·2	0·51	23	10·9	0·55	76	19·6	0·12	55	13·6	0·28
4·5–5·0	20	17·8	0·24	23	11·2	0·52	75	21·2	0·10	53	13·4	0·34
5·0–5·5	24	19·0	0·17		12·0	0·50	75	21·4	0·10	58	15·6	0·38
5·5–6·0	27	18·4	0·18		12·0	0·50	76	17·2	0·09	61	16·7	0·45
6·0–6·5	53	16·5	0·21		11·8	0·50	92	16·8	0·08	58	17·9	0·45
6·5–7·0	42	15·2	0·30	54	10·8	0·50	114	22·0	0·12	52	19·1	0·45
7·0–7·5	30	13·9	0·48		8·8	0·50	110	22·1	0·09	46^{A}	19·6	0·45
7·5–8·0	42	12·0	0·44		5·8	0·50				44	20·3	0·45
8·0–8·5	31	10·3	0·43		2·0	0·50				44	20·5	0·45
8·5–9·0	21	10·2	0·48	59	1·5	0·50				43	20·8	0·45
9·0–9·5	^{A}	9·3	0·50							41	20·8	0·45
9·5–10·0		8·5	0·50							38	20·7	0·45
10·0–11·0		7·5	0·50							36	18·3	0·45
11·0–12·0	55	6·0	0·50							41	14·6	0·45

^{A} Signifies position of water table at time of sampling.

Tritium was assayed as previously described (Hughes and Allison 1976), and chloride determined, either potentiometrically using standard silver nitrate solution or colorimetrically using mercuric thiocyanate and ferric nitrate (Zall *et al.* 1956). Chloride results were expressed in terms of concentration of chloride in the soil solution. Tritium results were expressed in tritium units.*

Results and Discussion

Tritium Measurements

The variation of TC with depth has been previously reported for four sites within the study area (Allison and Hughes 1974; Allison 1975) and at two of these, multiple coring was undertaken. At the remaining 12 sites, samples were collected from nine locations in March 1975 and from three in October 1975. The TC and water content data obtained at these sites are shown in Table 1.

Estimates of local recharge can be made most easily from the total amount of tritium held in the soil profile (Smith *et al.* 1970; Allison and Hughes 1974). This implies that sampling has been carried out to such a depth that the TC of soil water at the bottom of the hole is close to zero.

However, at none of our sites did the coring reach a great enough depth to obtain soil water with a TC near zero. However, since soil water usually moves downwards via piston flow below the root zone (Zimmerman *et al.* 1967), it is usually possible to identify the year in which recharge corresponding to water at the bottom of the sampled profile occurred. As well as this a peak in the TC *v.* depth profile corresponding to the 1964–65 peak in TC of rainfall in southern Australia (Allison and Hughes 1977) can usually be identified. The approaches which we used are as follows.

In those profiles where the 1964–65 peak could be identified, two techniques could be used for evaluating local recharge. Firstly, assuming piston flow, all of the tritium above this peak was added to soil since 1965; thus if sampling was carried out in March 1975, evaluation of the expression

$$T = \int_0^d T_z \theta_z \mathrm{d}z,$$

where d is the depth of the peak beneath the soil surface and T_z and θ_z are the TC and volumetric water content respectively at a distance z beneath the soil surface, yields the total quantity of tritium T added to the soil profile since 1965. If sampling takes place later than March (the time of maximum soil moisture deficit), a correction term, based on the net accession of tritium in the soil surface after March, must be subtracted from this integral to obtain the appropriate value of T (Allison and Hughes 1974). Assuming unit recharge each year, the amount of tritium T_{u} which would have been added to the profile since 1965 after allowing for decay is given by

$$T_{\mathrm{u}} = \sum_{n=1}^{10} W_n T_i(n) \exp(n\lambda),$$

where $T_i(n)$ is the input TC n years from the time of sampling, λ the decay constant for tritium ($0 \cdot 0565$ year^{-1}) and W_n a weighting function which takes year to year variation of recharge into account, where

$$\sum_1^n W_n = n.$$

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* One tritium unit is defined as one tritium atom in 10^{18} atoms of all hydrogen species.

The importance of this parameter is discussed later in this section. The MAR is then given by T/T_u.

Secondly, MAR can be obtained simply by estimating the total amount of water stored in the profile in March (the driest time of the year) between the surface and the 1964–65 peak in TC. MAR is obtained by dividing this by the number of years between 1964–65 and the time of sampling. At some of our sites, soil water samples were obtained to some depth below this peak. At these sites the year in which the soil water at the bottom of the profile fell as rain was estimated from its TC, thus enabling an additional estimate of MAR to be made. For the sites where sampling did not extend to the 1964–65 peak, rough estimates of annual recharge rates were made using estimates of the 'age' of water at the limit of sampling depth. These estimates of 'age' were obtained using the precipitation fallout pattern described previously (Allison and Hughes 1977).

Table 2. Estimates of mean annual recharge using tritium concentrations

Site no.[A]	Estimated from the amount of tritium above: The peak (mm)	Estimated from the amount of tritium above: The bottom of hole (mm)	Estimated from the amount of water above: The peak (mm)	Estimated from the amount of water above: The bottom of hole (mm)	Av. MAR (mm)
2	100	—	100	—	100
3	80	80	160	140	115
5	100		130		115
8	120		150		135
9	120	150	130	130	130
11	150	170	150	200	170
12	170	250	180	260	215
13	160	190	220	200	190
14	190	190	260	200	210
15					
16	240	300	270	260	270

[A] Results for those sites not given here have been published previously (Allison and Hughes 1974; Allison 1975).

Estimates of the MAR using as many of the approaches above as possible are shown in Table 2. In making these estimates we have assumed that the TC of precipitation is the same over the whole of the area studied. This is a reasonable assumption since the area has a low relief (nearly all of the area is less than 70 m above sea-level), and the TC of precipitation at Mt Gambier, near the centre of the area, and Cape Northumberland, on the coast, are virtually identical (Allison and Hughes 1977).

As stated earlier, estimates of MAR are required, but due to variations in rainfall and its seasonal distribution, recharge varies considerably from year to year. In a lysimeter experiment carried out in the swampy podzols, local recharge at one site varied between 25 and 134 mm year^{-1} for the period 1960–65 (Holmes and Colville 1970).

Other workers have used a range of weighting functions to assign the relative importance of the contribution of each year's recharge to the total tritium in the profile. Smith *et al.* (1970) used annual precipitation and estimates of evapotranspiration, while Bredenkamp *et al.* (1974) and Atakan *et al.* (1974) used observations of fluctuations of groundwater levels to do this. The latter authors compared this method of weighting with a method using the variation of precipitation in the recharge season, and concluded that water level changes provided the best method.

In earlier work Allison and Hughes (1974) found that recharge estimates were not greatly affected by the weighting function used. However, because some of our later profiles intersect relatively few years recharge, we have tested three different weighting schemes. Those tried were based on: (1) the amount of winter rainfall $W_n = P_w(n)/\bar{P}_w$, where $P_w(n)$ is the winter rainfall in year n; (2) groundwater level fluctuations $W_n = \Delta h(n)/\Delta\bar{h}$, where $\Delta h(n)$ is the difference between maximum and minimum groundwater level in year n; and (3) an empirical relationship $W_n = (P_w(n) - C)/(P_w - C)$, where C is a constant based on evapotranspirationl loss from the soil store (Allison and Hughes 1974) and = 260 when P_w is expressed in millimetres. The performance of these weighting schemes is shown graphically in Fig. 2 for 1965–74, the period for which groundwater levels are available (F. W. Aslin, private communication 1976). It was found that, although the functions sometimes give different weights to each year's recharge, there is little difference in the total tritium added to a soil profile for unit recharge over a period of several years. For example, for the period 1965–1974, the calculated amounts of tritium stored in the soil using the three weighting functions are 1·88, 1·89 and 1·85 TU m respectively. If W_n is assumed to be unity, a value of 1·91 TU m is obtained. Similar agreement is obtained for time intervals as short as 6 years or as long as 20 years. Since quite different weighting schemes give almost identical values for T_u for southern Australia, it was considered unnecessary to use other than unit weights in our calculations.

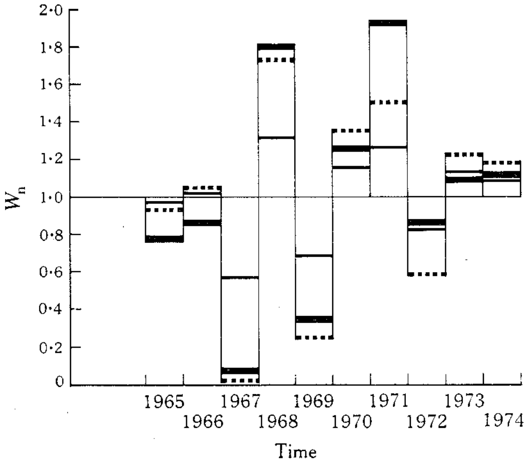

Fig. 2. Comparison of weighting schemes used to assess the importance of annual variations in recharge.
Thin rule: $W_n = P_w(n)/\bar{P}_w$.
Thick rule: $W_n = \Delta h(n)/\Delta\bar{h}$.
Broken rule:
$W_n = [P_w(n) - 260]/(\bar{P}_w - 260)$.

In addition to the problem of assigning weights to each recharge increment, it is important to know if the tritium record over the fairly short period intercepted by our sampling (6–20 years), will provide a reasonable estimate of the long term MAR. As evidence that values of MAR obtained from our tritium profiles are close to the long-term mean, the mean winter rainfall, $\bar{P}_w$, was determined for time intervals of similar length to that of the tritium record in our soil profiles, and compared with the long-term value of $\bar{P}_w$. For Mt Gambier Airport, $\bar{P}_w$ for the period 1942–74 is 479 mm, while that for the periods 1956–74, 1965–74 and 1969–74 are 462, 459 and

464 mm respectively. Since the means for the time intervals of interest to us are 3–4% lower than the long term mean, it is possible that the estimates of MAR made using the tritium record in the soil may be slightly lower than the long term MAR.

The importance of the land use being constant over at least the time period used to obtain an estimate of the MAR can be seen by the results from site 15 (Table 1). It was discovered after sampling and analysis that *Pinus radiata* had been grown at this site only a few years previously. The recharge beneath this vegetation is known to be lower than that beneath pasture (Allison and Hughes 1972), and this offers an explanation of the low estimate of recharge found. Similar difficulties are discussed in the next section.

Chloride Measurements

In studies aimed at the determination of MAR using chloride, it is assumed that the only source of chloride is at the soil surface, either in precipitation or as dryfall, and that there is no contribution of chloride from weathering. In the well-drained soils of this area this appears to be a reasonable approximation. An important source of chloride in addition to precipitation is that of applied fertilizers, particularly potassium chloride. Records of fertilizer applications were available for most of our sites. At two sites it was necessary to take these into account in our calculations of recharge. The only chloride removed from the sites is that held in the body tissues of livestock and is therefore negligible.

Hutton (1976) has summarized what is known of the relationship between chloride fallout and distance from the coast in south-eastern Australia. We have used his empirical relationship (equation 1) to estimate the mean annual chloride concentration of rainfall, $\bar{C}_{\mathrm{p}}$ (m.e. l^{-1}), at our sampling sites:

$$\bar{C}_{\mathrm{p}} = 0\cdot 99/\sqrt[4]{d}-0\cdot 23. \tag{1}$$

The distance from the coast, d, is measured in kilometres in the direction most likely to contribute maximum oceanic chloride. In our case, this is south-west.

Equation (1) does not take salt fall by impingement into account, but does include dryfall as the samples were collected in rain gauges exposed for the whole year and not only when rain was falling.

Because roots of pasture plants remove water from the soil down to 2 m, only chloride concentrations below this depth represent that of recharge water. To obtain average values of the chloride concentrations of recharge water, values for several depth intervals were usually averaged. However, when the chloride concentration of water samples taken from the top of the water table were available, these were used in preference to those of the soil solution.

On average, the flux of chloride through the soil surface is equal to the flux of chloride beneath the root zone, thus

$$\overline{PC}_{\mathrm{p}} = \overline{RC}_{\mathrm{R}}, \tag{2}$$

where P is the annual rainfall of chloride concentration C_{p} and R the recharge flux of chloride concentration C_{R}. From Hutton's data (Hutton 1957, 1962), it can be seen that the flux of chloride at the soil surface is approximately constant from year to year (i.e. when P is high, C_{p} is lower than $\bar{C}_{\mathrm{p}}$ and vice versa). Because the chloride data used to derive equation (1) were obtained over a period of near average rainfall (Hutton 1957, 1962), values of $\overline{PC}_{\mathrm{p}}$ for each site were obtained by multiplying C_{p} (from equation (2)) by the appropriate value of $\bar{P}$.

Since $\overline{RC}_R = \bar{R}\bar{C}_R + \overline{\Delta R \Delta C}_R$ where ΔR and ΔC_R are deviations of the annual values of R and C_R from the annual means, equation (2) becomes

$$\overline{PC}_p = \bar{R}\bar{C}_R + \overline{\Delta R \Delta C}_R;$$

thus

$$\bar{R} = (\overline{PC}_p - \overline{\Delta R \Delta C}_R)/\bar{C}_R. \tag{3}$$

Some negative correlation is expected between R and C_R (high R being associated with low C_p and vice versa), thus $\overline{\Delta R \Delta C}_R$ is expected to be negative and non-zero. To obtain an estimate of the magnitude of this term, the weighting schemes used in the previous section were used to give an indication of the way in which R might vary from year to year (and hence give an assessment of ΔR). Inspection of the chloride profiles shows that below 2 m (the bottom of the root zone) the variation of chloride concentration about the mean is rarely more than 30% and usually less. Assuming ΔC_R falls within the range $+0{\cdot}3\bar{C}_R$ to $-0{\cdot}3\bar{C}_R$, $\overline{\Delta R \Delta C}_R$ is found to be 10–15% of $\overline{RC}_R$. Values of MAR, calculated assuming $\overline{\Delta R \Delta C}_R = 0{\cdot}1\overline{RC}_R$, are given in Table 3.

Table 3. Estimates of mean annual recharge using chloride concentrations

Site no.	Annual precipitation (mm)	Chloride concn. of precipitation[A] (mg l^{-1})	Mean chloride concn. of soil solution (mg l^{-1})	Recharge (assuming $\overline{\Delta R \Delta C_R} = 0{\cdot}1\overline{PC_P}$) (mm)
1	740	6·7	73	70
2	740	8·4	65	100
3	760	6·7 (7·9)[B]	84	140
5	740	8·1	64	100
6	740	8·8	67	110
8	710	6·3 (3·7)[B]	51	150
9	740	12·6	73	140
11	710	6·3	35	140
12	740	6·7	23	240
13	740	6·7	30	180
14	740	6·7	21	260
15	740	12·6	91	110[C]
16	740	12·6	41	250

[A] Estimated using equation (1).
[B] Chloride added in fertilizer (expressed as mg l^{-1} in precipitation; see text).
[C] Discarded due to change in land use.

At sites 3 and 8 chloride which has been added as fertilizer was accounted for by adding the annual input of chloride in the fertilizer to the chloride flux at the soil surface.

Table 3 gives the chloride data for our sites together with estimates of recharge using this technique.

In some profiles (for example, sites 1 and 9) a peak of up to 300–400 mg l^{-1} occurred in the chloride profile, while the water draining from the soil had a concentration of approximately 70 mg l^{-1}. Since these soils were formed in the late Pleistocene, it is unlikely that any chloride is still being removed from the matrix by leaching. A possible explanation of this peak in chloride could be made on the basis of that proposed by Blackmore (1976), who suggested that water may be able to diffuse in and out of pores with small openings, but that chloride, being partially hydrated and hence larger, cannot. Thus HTO which moves in a similar way to water can diffuse through the whole matrix; for this reason the tritium profiles show the expected shape with no distortion due to the presence of non-labile water in the matrix.

This difficulty occurred only on the more clayey soils, and at these sites the chloride analyses used were those of water samples taken beneath the water table or of soil water in the lighter-textured parts of the profile.

As with the interpretation of tritium data, uniform land use must be assumed for sufficient time to allow enough water to move through the soil to establish a new equilibrium chloride profile at least to the depth at which measurements are made.

The importance of change in recharge rate and hence chloride concentration due to change in land use is shown by data from sites 13 and 14, where the chloride concentration of groundwater 4 m beneath the water table increases from 30 mg l^{-1} to 60 mg l^{-1}. This difference is possibly due to a change in land use which occurred when bracken (*Pteridium esculentum*), a deep-rooted summer-growing species, was replaced with mixed perennial pasture. The latter is expected to establish a smaller soil moisture deficit allowing a higher recharge.

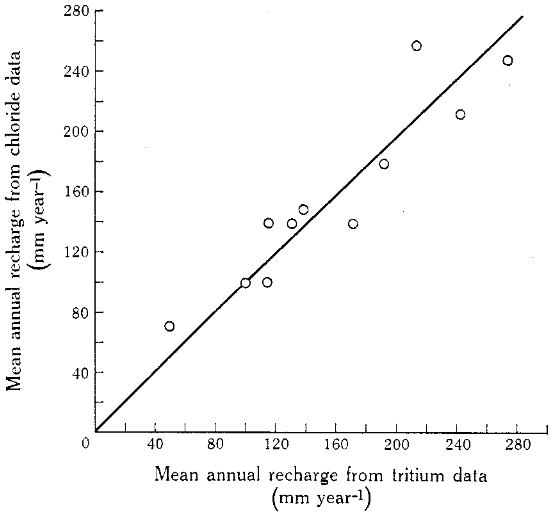

Fig. 3. Comparison of recharge estimates obtained from chloride and from tritium data.

Total Recharge to the Area

In Fig. 3 estimates of recharge made using tritium are compared with those made using chloride. Good agreement is evident between the estimates made using the two techniques. The data also provide evidence that the equation derived by Hutton (1976) describes net chloride fallout in the area studied.

In using the techniques described in this paper to estimate total MAR to a region, it is assumed that recharge is uniform over quite large areas. In a study of recharge to an area of some thousands of km², Sukhija and Shah (1976) found that point estimates of MAR made from tritium measurements gave similar estimates of MAR as those produced by a mathematical model describing water movement within the underlying aquifer. Our sampling program also provides evidence that, at least for our soils, recharge is uniform over quite large areas, since when several estimates of MAR were obtained for one hydrologic unit they were in good agreement with each other. For example, in the aeolianite, MAR, estimated using tritium, was 170, 190, 210 and 215 mm year^{-1} at the four sites.

To obtain total recharge occurring through each hydrologic unit, the mean recharge obtained for all sites within each unit was multiplied by the area of that unit. The components of the water balance of the area are shown in Table 4. The total MAR to the area shown in Fig. 1 is estimated to be $2 \cdot 4 \times 10^8$ m^3 year^{-1} using the tritium data and $2 \cdot 3 \times 10^8$ m^3 year^{-1} using the chloride data.

Table 4. Estimates of mean annual recharge for the various hydrologic units

Hydrologic unit	Site no.	Area (km^2)	Mean annual recharge (mm) Estimated using chloride	Mean annual recharge (mm) Estimated using tritium
Sand over heavy clay	1	157	70	50
Volcanic soils	2	21	100	100
Sand over sandy clay	3, 4	52	140	100
Sand over thin sandy clay over limestone	5, 6	49	105	120
Terra rossa over limestone	7, 8	60	150	130
Thin sandy loam over limestone	9, 10	281	140	155
Aeolianite	11, 12, 13, 14	380	200	195
Skeletal soils	15, 16	330	250	270

These values are higher than the earlier recharge estimate made using very limited data and a smaller area (Allison 1975). Using the boundaries as drawn in the earlier paper, the MAR obtained is $1 \cdot 7 \times 10^8$ m^3 year^{-1} compared with $1 \cdot 5 \times 10^8$ calculated at that time.

Waterhouse (1975) has estimated subsurface flow beneath 27 km of coastline as between $0 \cdot 2$ and $0 \cdot 4 \times 10^8$ m^3 year^{-1}. For our area the length of coastline is 40 km, and the estimated limits of subsurface flow are $0 \cdot 2$ and $0 \cdot 7 \times 10^8$ m^3 year^{-1}. Urban and irrigation use is approximately $0 \cdot 2 \times 10^8$ m^3 year^1 and discharge from swamps due to springs and local surface run-off is $1 \cdot 6 \times 10^8$ m^3 year^{-1} (Allison 1975). A component of groundwater discharge, neglected in the previous paper, is evapotranspiration from the phreatophytes growing in the coastal swamps. A simple water balance using an evapotranspiration of 1000 mm year^{-1}, a precipitation of 750 mm year^{-1} and an area of 49 km^2 gives a total loss of water from the swamps due both to discharge and evapotranspiration of $1 \cdot 7 \times 10^8$ m^3 year^{-1}. If the upper limit of Waterhouse's (1975) values for subsurface discharge is used, the total discharge for the area is $2 \cdot 6 \times 10^8$ m^3 year^{-1}, which is in good agreement with our estimate for total MAR for the area. It should be noted that the estimate of subsurface discharge may be considerably in error as there is only very limited information available on aquifer properties near the coast.

Errors

This water balance has ignored any leakage of water from or to the underlying Knight Group aquifer. Some movement of water may occur from the Knight Group to the Gambier Limestone in the region of Mt Gambier, where some faulting has taken place and the potentiometric level of water in the Knight Group is higher than that in the Gambier Limestone. Recharge through the base of swamps which cover a small portion of the area is also ignored. This is unlikely to be a major component of the water balance.

In earlier work at two locations where multiple sampling was undertaken, the relative standard deviation (RSD) of the recharge estimate using the technique used here, was found to be 15% (Allison and Hughes 1974). Similar estimates of standard deviation are not available for the chloride profiles. This estimate of RSD was made using estimates of MAR obtained from tritium profiles only, and does not include deviation arising from the tritium input function. Because of this, the errors given below are minimum values.

If it is assumed that the MAR of each hydrologic unit has a RSD of 15%, the standard deviation for the total recharge (as estimated using tritium) is $0\cdot2\times10^8$ m^3 year^{-1}. However, this estimate of error assumes that there is no error in the positioning of boundaries between the hydrologic units.

Over much of the study area, error in positioning the boundaries will not have a large effect on the total MAR, since, with two exceptions, recharge does not vary greatly from hydrologic unit to hydrologic unit. The boundary which is most susceptible to error is that between the skeletal soils and sandy loams, and the difference in estimated MAR between these two units is 110 mm year^{-1}. If the area of sandy loams is over- or underestimated by 20%, then the MAR for the study area is approximately 3% low or high. An additional source of error arises in defining the streamline boundaries of our study area. This error is unlikely to be greater than 5%. The total standard deviation is likely to be approximately $0\cdot3\times10^8$ m^3 year^{-1}.

The methods for estimation of recharge described in this paper rely on the measurement of an amount (tritium) or a concentration (chloride). Thus in the case of tritium, sampling and analytical errors will become less important as recharge increases. However, since recharge is inversely related to chloride concentration, sampling and analytical errors will become less important at high recharge rates. Thus chloride should provide the best estimates of MAR at low values of MAR and tritium at high values of MAR.

Conclusions

The agreement which has been obtained between estimates of recharge made using chloride and tritium at a range of sites suggests that chloride could be profitably used more often as a tracer in hydrologic studies. Compared with tritium, it has the advantage of simple analysis, but, as with tritium, information about fallout and land-use changes at the sampling sites is essential.

The agreement between the inflow and outflow components of the water balance found here suggests that the estimate of total recharge given above provides a reasonable basis for planning the exploitation of the water resource.

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References

Allison, G. B. (1975). Estimation of the water resources of a portion of the Gambier Plain using a new method for evaluation local recharge. Proc. Hydrol. Symp., pp. 1–5, Armidale, May 1975 (Inst. Eng., Aust.: Sydney.)

Allison, G. B., and **Hughes, M. W.** (1972). Comparison of recharge to groundwater under pasture and forest using environmental tritium. *J. Hydrol.* **17**, 81–95.

Allison, G. B., and **Hughes, M. W.** (1974). Environmental tritium in the unsaturated zone; estimation of recharge to an unconfined aquifer. Proc. Symp. Isotope Techniques in Groundwater Hydrol. Vol. 1, pp. 57–72. (I.A.E.A., Vienna.)

Allison, G. B., and **Hughes, M. W.** (1977). The history of tritium fallout in southern Australia as inferred from rainfall and wine samples. *Earth Planet Sci. Lett.* **36**, 334–40.

Anderson, V. G. (1945). Some effects of atmospheric evaporation and transpiration in the composition of natural waters in Australia (continued). 4. Underground waters in riverless areas. *J. Aust. Chem. Inst.* **12**, 83–98.

Anderson, L. J., and **Sevel, T.** (1974). 6 years environmental tritium profiles in the unsaturated and saturated zones, Gronhoj, Denmark. Proc. Symp. Isotope Tech. in Groundwater Hydrol. Vol. 1, pp. 3–20. (I.A.E.A., Vienna.)

Atakan, Y., **Roether, W.**, **Munnick, K. O.**, and **Matthess, G.** (1974). The Sandhaussen shallow groundwater tritium experiment. Proc. Symp. Isotope Tech. in Groundwater Hydrol. 1974. Vol. 1, pp. 21–43. (I.A.E.A., Vienna.)

Blackburn, G. (1959). Soils of County Grey, South Australia. CSIRO Aust. Soils Land Use Ser. No. 33.

Blackmore, A. V. (1976). Salt sieving within clay aggregates. *Aust. J. Soil Res.* **14**, 149–58.

Bredenkamp, D. B., **Schutte, J. M.**, and **Dutoit, G. J.** (1974). Recharge of a dolomite aquifer as determined by tritium. Proc. Symp. Isotope Techniques in Groundwater Hydrol. 1974. Vol. 1, pp. 73–94. (I.A.E.A., Vienna.)

Colville, J. S., and **Holmes, J. W.** (1972). Water table fluctuations under pasture and forest in a Karstic region of South Australia. *J. Hydrol.* **17**, 61–80.

Eriksson, E., and **Khunakasem, V.** (1969). Chloride concentration in groundwater, recharge rate and rate of deposition of chloride in the Israel Coastal Plain. *J. Hydrol.* **7**, 178–97.

Holmes, J. W., and **Colville, J. S.** (1970). Grassland hydrology in a karstic region of southern Australia. *J. Hydrol.* **10**, 38–58.

Hughes, M. W., and **Allison, G. B.** (1976). Improved techniques for the estimation of the natural abundance of tritium. CSIRO Aust. Div. Soils Tech. Pap. No. 29.

Hutton, J. T. (1957). Rainwater analysis. CSIRO Div. Soils, Div. Rep. 8/57.

Hutton, J. T. (1962). Rainwater analysis July 1957 to March 1961. CSIRO Div. Soils, Div. Rep. 7/62.

Hutton, J. T. (1976). Chloride in rainwater in relation to distance from ocean. *Search* **7**, 207–8.

Peck, A. J., and **Hurle, D. H.** (1973). Chloride balance of some farmed and forested catchments in Southwestern Australia. *Water Resour. Res.* **9**, 648–57.

Smith, D. B., **Wearn, P. L.**, **Richards, H. J.**, and **Rowe, P. C.** (1970). Water movement in the unsaturated zone of high and low permeability strata by measuring natural tritium. Proc. Symp. Isotope Hydrol. 1970, pp. 73–87. (I.A.E.A., Vienna.)

Sukhija, B. S., and **Shah, C. R.** (1976). Conformity of groundwater recharge rate by tritium method and mathematical modelling. *J. Hydrol.* **30**, 167–8.

Waterhouse, J. D. (1975). The hydrogeology of the Mount Gambier area, south-eastern South Australia. Dep. Mines S.A. Rep. Book No. 75/82.

Zall, D. M., **Fisher, D.**, and **Garner, M. O.** (1956). Photometric determination of chloride in water. *Analyt. Chem.* **28**, 1665–8.

Zimmerman, U., **Munnich, K. O.**, and **Roether, W.** (1967). Downward movement of soil moisture traced by means of hydrogen isotopes. Geophys. Monogr. Am. Geophys. Union, No. 11 (Ed. G. E. Stout), p. 28.

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