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Catchment conceptualisation for examining applicability of chloride mass balance method in an area of historical forest clearance

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Abstract

Among various approaches for estimating groundwater recharge, chloride mass balance (CMB) method is one of the most frequently used, in particular, for arid and semiarid regions. Widespread native vegetation clearance, common history in many areas globally, has changed land surface boundary condition, posing a question whether the current system has reached new chloride equilibrium for CMB application. To examine CMB applicability for catchments, conceptual catchment types of various chloride equilibrium conditions are defined. The conceptualization, combined with some local climate conditions, is demonstrated to be useful in examining whether a catchment has reached new chloride equilibrium. The six conceptual catchment types are tested with eleven selected catchments in the Mount Lofty Ranges (MLR), a coastal hilly area in South Australia having experienced historical widespread forest clearance. The results show that six of the eleven catchments match type VI chloride balance condition (chloride non-equilibrium with a gaining stream), with the ratio of stream chloride output over atmospheric chloride input (catchment chloride O/I) ranging from 2 to 4. Two catchments match type V chloride balance condition (chloride non-equilibrium with a losing stream), with catchment chloride O/I values about 0.5. For these catchments, the CMB method is not appropriate to apply. The results also suggest that neither a below-one chloride O/I value nor a low seasonal fluctuation of streamflow chloride concentration (a factor below 4) guarantees a chloride equilibrium condition in the study area. But a large chloride O/I value (above one) and a large fluctuation of streamflow chloride concentration (a factor of 10 and above) generally indicates either a chloride disequilibrium, or cross-catchment water transfer, or both, for which CMB is not applicable. Based on the regression between chloride O/I values and annual precipitation for type VI catchments, a catchment with annual precipitation of 900 mm in MLR has most likely reached new chloride equilibrium, for which CMB can be applied given that no cross-catchment water transfer occurs. CMB is applied for one catchment at chloride equilibrium, resulted in a net groundwater recharge estimate of 30 mm, about 4%

of annual precipitation.

1 Introduction

Among various approaches for estimating groundwater recharge, chloride mass balance (CMB) method is one of the most frequently used, especially for arid and semi-arid regions (Petheram et al., 2002; Scanlon et al., 2002; Wilson and Guan, 2004). The basic idea of the CMB method is that the atmospheric input of chloride with precipitation water is left and concentrated in the residual soil water via evapotranspiration processes. By measuring chloride concentration in the soil water, or the resulted groundwater, we can then estimate the (potential) recharge rate. The CMB method can be applied to saturated zone (Eriksson and Khunakasem, 1969; Dettinger, 1989; Wood and Sanford, 1995), or unsaturated zone (Walker et al., 1991; Cook et al., 1992; Phillips, 1994; Scanlon and Goldsmith, 1997; Edmunds et al., 2002). Because of the complexity in both hydro geological and hydrometeorological aspects, the CMB application in the unsaturated zone is not recommended for estimating groundwater recharge in mountains (Wilson and Guan, 2004). Application of the CMB method in the saturated zones is commonly used to estimate mountain front (or block) recharge (Wilson and Guan, 2004; Wahi et al., 2008; Ma et al., 2009).

When it is applied in mountain areas, the CMB method is applied over a catchment. Major assumptions of the CMB method include (1) groundwater recharge rate of the interest area is constant and in equilibrium with near-surface and atmospheric conditions in terms of both water and chloride fluxes; (2) the atmospheric chloride input rate over the area is constant and is known. Other additional assumptions can be found in (Wood, 1999). It is important and critical to check both listed assumptions when the CMB method is applied, in particular, for the areas of significant land use changes, such as the coastal areas of Australia.

Similar to the situations in many other countries, coastal areas of Australia house a large portion of population and economic activities. A good quantification of water resources in these areas, including groundwater recharge, is critical for various aspects of economic and societal development. Mountainous and hilly terrains in Australian coastal areas enhance precipitation, providing a large amount of water resources to the area. With the increasing awareness of climate change impact on water resource sustainability, estimates of groundwater resources become more urgent. Because of its simplicity, the CMB method is the first recharge-estimating approach to be considered. However, two challenging problems related to the above two assumptions need to be resolved when the CMB method is attempted. First, widespread native vegetation clearance for agriculture since European settlement about 150 years ago has changed land surface boundary condition, posing a question whether the current system has reached new chloride equilibrium condition for the CMB application. Another challenge is that the spatial variability of atmospheric chloride input is large in coastal areas, leading to a big problem to reliably estimate atmospheric input chloride. The second issue has been recently addressed for the Mount Lofty Ranges (MLR) in South Australia (Guan et al., 2009a). The focus of this present paper is to examine the first issue, i.e., whether the MLR catchments have reached new chloride equilibrium.

Impacts of vegetation clearance on catchment water chemistry have been noticed for decades (Peck and Hurle, 1973; Likens et al., 1978; Williamson et al., 1987). These and some other studies were performed mainly from the aspect of dry land salinity issues (Jolly et al., 2000; Kayaalp and Bye, 2003; Poulsen et al., 2006). Few of them were directly linked to CMB application. As catchment stream chloride (salt) load changes after clearance, and will eventually reach a new equilibrium status, examination of catchment chloride budget may provide valuable information for revealing catchment chloride equilibrium status (i.e., how far from the new equilibrium). Surprisingly, no conceptual model has been proposed in literature to represent different catchment chloride equilibrium conditions. The primary objectives of this study are (1) to conceptualize catchment chloride equilibrium conditions and their quantitative indicators, and (2) to demonstrate how these conceptual models, combined with climate information, are useful to examine whether a catchment has reached new chloride equilibrium for the CMB application, and (3) to identify the catchments in a coastal hilly region of South Australia that are valid for CMB application, and estimate catchment groundwater recharge.

2 Conceptual models of catchment chloride equilibrium conditions

The idea of using catchment chloride budget for testing CMB applicability is based on the assumption that different catchment chloride equilibrium status are quantitatively distinguishable. Based on some previous studies, the ratio of the catchment chloride mass loss through streamflow over the total chloride mass input from atmospheric deposition (denoted as chloride O/I ratio hereafter) can be a useful quantitative indicator. An equivalent quantity for water is also used in the paper. Water O/I is defined as the ratio of annual streamflow exporting water out of the catchment over annual precipitation bringing water into the catchment. Chloride O/I ratios have been observed increasing after forest clearance. Peck and Hurle (1973) examined 15 catchments of various sizes within 150 km from the coast in southwest Western Australia, among which eight were forested, and seven were partially cleared (within the past 150 years) farmland. Their results show that in the forested catchments, the salt O/I value is about 1 to 1.6, while for the cleared farmland, the ratio spreads from 3 to 21. In the MLR of South Australia where widespread forest clearance occurred after European settlement, Williamson and van der Wel, (1991) examined the salt O/I ratio for 21 selected catchments, and found that 19 out of the 21 have salt O/I between 3 to 9. These observations suggest that vegetation clearance breaks down catchment water and salt (chloride) equilibriums that were established under the pre-clearance conditions, and that the catchment chloride O/I value can be a quantitative indicator inferring chloride equilibrium status.

This idea of using chloride O/I for determining catchment chloride equilibrium status is demonstrated in the six conceptual catchments (Fig. 1). Two catchment types (I and II) are chloride equilibrium conditions for which CMB can be applied for estimating groundwater recharge, two (type III and IV) are in chloride equilibrium but contaminated by cross-catchment chloride transfer, and two (types V and VI) are non-equilibrium conditions, for which CMB is not applicable. For easy discussion, two recharge quantities are defined. One is catchment-average vertical direct water-table recharge, denoted as R. The other is net catchment groundwater recharge, denoted as R_n, which is the water-table recharge less groundwater discharge through based flow into the stream, measured at the outlet point of the catchment. It is important to make such distinction. Using direct water-table recharge for the catchment will overestimate the total amount of groundwater available for water resource allocation.

For a type I catchment, with losing streams, catchment chloride mass balance follows

$$P \cdot C_p = R \cdot C_R + q_e \cdot C_e \tag{1}$$

where C_p is chloride concentration in bulk precipitation, P is precipitation in the catchment, C_R is chloride concentration in direct water-table recharge R, q_e is the event flow, and C_e is chloride concentration of the event flow. Because of no base flow occurring, chloride in recharge groundwater from the catchment does not return to the surface. Net catchment recharge is equal to water table recharge, and can be estimated by

$$P \cdot C_P = R_n \cdot C_R + q \cdot C_q \tag{2}$$

where C_q is chloride concentration in the stream runoff q that carries water out of the catchment. As only part of atmospheric chloride deposition is exported out of catchment by event flow, the chloride O/I is smaller than one (Fig. 1 I).

For a type II catchment (Fig. 1 II), part or all of recharge groundwater and its bearing chloride come back to the surface, and is exported out of the catchment. The catchment chloride balance follows Eq. (1). Chloride in the stream water is composed of that in both event flow and base flow,

$$q \cdot C_q = q_e \cdot C_e + q_b \cdot C_b \tag{3}$$

where q_b is the base flow, and C_b is chloride concentration of the base flow, other symbols are defined previously. Net catchment recharge is smaller than water-table recharge, and can be estimated by Eq. (2) with an assumption that chloride concentration in base flow water is the same as that in the direct recharge groundwater. In a type II catchment, the chloride O/I value can be smaller than or equal to one.

Type III and type IV catchments (Fig. 1 III and IV) are those influenced by cross-catchment water transfer, with type III having surface water transfer, and type IV having subsurface water transfer. Chloride in the stream water is the sum of that from event flow, base flow, and cross-catchment transfer water,

$$q \cdot C_q = q_e \cdot C_e + q_b \cdot C_b + T \cdot C_T \tag{4}$$

where T is the cross-catchment transfer water flow, and C_T is the chloride concentration in the cross-catchment transfer water. The chloride O/I ratio most likely exceeds one, depending on the relative amount of transferring water. Water O/I of a type III or IV catchment is significantly larger than that of a type I or II catchment. Generally, the CMB method is not applicable for a type III or IV catchment. However, if the surface water transfer is quantified, net catchment groundwater recharge can be estimated for a type III catchment by Eq. (5), with assumption that C_b is equal to C_R.

$$P \cdot C_P + T \cdot C_T = R_n \cdot C_R + q \cdot C_q \tag{5}$$

where the symbols are described previously. In a type IV catchment, cross-catchment water and chloride inputs occur in subsurface. If these fluxes locate in depth and do not affect shallow groundwater and stream water, they can be neglected. The catchment can be regarded as a type II catchment. Otherwise, the CMB method is not applicable.

Type V and VI catchments (Fig. 1 V and VI) represent post-clearance situations, in which historical chloride accumulated in the vadose zone under pre-clearance conditions is now released into groundwater and surface water. Catchment chloride balance is described by

$$P \cdot C_P + S = R \cdot C_R + q_e \cdot C_e \tag{6}$$

where S is re-mobile historical soil chloride. For a type V catchment, base flow is missing, the chloride O/I ratio is likely smaller than one because of little horizontal subsurface flow that brings soil chloride into the stream. In a type VI catchment, base flow and horizontal subsurface flow deliver historical chloride into the stream, the chloride O/I is larger than one. As catchment chloride is not in equilibrium with current surface and atmospheric conditions in a type V or VI catchment, the CMB method is not applicable for either of them.

Lets now examine the conceptual catchments with some published observations. Williamson et al. (1987) studied 5 catchments in southwest Western Australia over 10 years. Among the five catchments they studied (Table 1), with assumptions that the forested catchments are in chloride equilibrium, and the cleared catchments are in disequilibrium after recent clearance, type I condition is observed in Ernies. Salmon represents type II or IV condition. Type VI condition is observed for Wights, and type V condition occurs in Dons and Lemon.

How are the conceptual catchment types and chloride O/I values used to determine CMB applicability? The CMB method generally does not apply for a catchment with chloride O/I ratio larger than one. If cross-basin chloride transfer is excluded, a chloride O/I value much larger than one is a good indicator of chloride non-equilibrium with current surface and atmospheric conditions. As chloride O/I value can be below one for both equilibrium and non-equilibrium conditions, it is difficult to determine whether the CMB method applies for a catchment with chloride O/I being smaller than one. In this situation, climate information may be incorporated to answer the question. Generally, it takes longer time for a catchment to reach new chloride equilibrium in a drier climate. For example, in the southern half of the Murray-Darling basin of Australia, the time for new salt equilibrium after clearance is approximately 90 years for a catchment with annual rainfall over 900 mm, and is over 300 years in an area of 600–750 mm annual rainfall (Jolly et al., 2001). This climate-dependent catchment chloride response can be incorporated to determine CMB applicability. For the three cleared catchments in Table 1, Wights is not in equilibrium, indicated from a chloride O/I ratio of 9.8. The other two catchments (Dons and Lemon), with vegetation cleared at the same time as Wights, are not in steady state yet because they are drier than Wights. More details are described in Sect. 3.3.

3 Methodology

3.1 Study area and data

Eleven catchments in the MLR of South Australia are selected to examine the catchment chloride equilibrium conditions. The MLR lies to the east of Adelaide, South Australia (Fig. 2). It covers an area of about 9000 km^2, with topographic relief of 700 m. The climate is of Mediterranean type. Annual precipitation ranges from below 300 mm to above 1000 mm (Guan et al., 2009b). Widespread vegetation clearance occurred during the European settlement some 100 to 150 years ago, which has dramatically altered surface condition, and broken pre-clearance catchment chloride equilibrium. Have the catchments reached new chloride equilibrium? This is an urgent practical question needed to be answered before the CMB method is used to estimate groundwater recharge. Actually, because of its simplicity, CMB has been applied for local and regional water resource allocations in the area (Banks et al., 2007; Green et al., 2007). Besides land use change, cross-catchment water transfer and reservoirs have modified local hydrology, including both water and chloride balance. Over the area, 15 reservoirs exist, and three main pipe lines convey water from a nearby river (Murray River in Fig. 2) to the MLR. These constructions add more complexity to challenge the CMB applicability. To avoid this complexity, eleven catchments without upstream reservoirs are carefully chosen. For ten of them, no pipe line outlets exist in the catchment, with one exception (catchment 7 in Table 2) to examine cross-catchment water transfer effect on chloride balance. Both daily streamflow and electrical conductivity (EC) data of each catchment are downloaded from http://e-nrims.dwlbc.sa.gov.au/swa/, and summarized in Table 2. As no chloride concentration was measured for time-series streamflow, relationship between chloride concentration and EC is developed based on about 450 point measurements conducted by the Department of Water, Land and

Biodiversity Conservation (DWLBC), and the Environmental Protection Agency (EPA), of South Australia. The sampling distribution is shown in Fig. 2. An annual chloride deposition map was adopted from (Guan et al., 2009a). Annual precipitation map was adopted from (Guan et al., 2009b). Some groundwater chloride data are used to estimate groundwater recharge after the CMB applicability is tested. Locations of these samples are shown in Fig. 2. Majority of the data are from (Radke et al., 2000), and some are from (Green et al., 2007).

3.2 Chloride budget calculation

Chloride and water input are calculated from the existing mean annual chloride deposition map and mean annual precipitation map for each catchment. Both maps have a spatial resolution of 1 km. The maps are clipped with the catchment boundary (Fig. 2) using ARCGIS toolbox. Total rainfall and chloride deposition are then calculated with the clip maps. Chloride and water output are calculated from measurements collected at the outlet point of the catchment. Average annual streamflow and its chloride load are calculated from measured daily streamflow and EC data for the years in which both data are available. In case some measurements (less than 10%) were missing in a month, average values of the month are applied for the missing days. For the study area, power-law relationship between streamflow chloride concentration and EC data is found (Fig. 3), which is applied to convert EC data into chloride concentration for all eleven catchments.

3.3 Relating chloride equilibrium status and climate condition

How is catchment chloride budget used to determine whether or not the CMB method applies? As both chloride equilibrium (types I and II) and disequilibrium (type V) catchments can have a chloride O/I value below or equal to one, it is difficult to tell type V catchments from type I and II catchments solely based on chloride O/I values. Type VI catchments have chloride O/I values larger than one, which are easier to be distinguished from type I and II catchments. They are distinguishable from type III and IV catchments by appearance of cross-catchment water transferring facility, or by water O/I values. Type III and IV catchments usually have a much larger water O/I ratio than a type V or VI catchment. With assumption that under a similar climate condition, type V catchments have similar chloride equilibrium status as type VI catchments that were experienced similar historical forest clearance, the relationship developed from type VI catchments, between chloride equilibrium status and some climatic/hydrological variables, applies to type V catchments.

To demonstrate how this works, lets imagine what happen to type II catchments with vegetation clearance. After vegetation clearance, they become type VI. Because of different local climate conditions, these type VI catchments will experience different evolution paths toward the new equilibrium status, i.e., back to type II catchments (Fig. 4). Catchment chloride O/I value is a good indicator of the chloride equilibrium status of type II/VI catchments. At a certain time point, chloride O/I values can be examined for all type VI catchments of various climate conditions (Fig. 4). Although it is difficult to tell for how long each of these catchments will reach new chloride equilibrium for CMB application, it is possible to tell under what conditions, a catchment has currently reached chloride equilibrium. This information is exactly what is needed for applying CMB method to estimate groundwater recharge. Correlation and regression analysis between chloride O/I and climate variables (precipitation), as well as other selected variables, are performed to find out the relationship between them. This relationship can then be used to examine chloride equilibrium status of a catchment which experienced similar forest clearance history.

4 Results and discussion

4.1 Catchment chloride budget

Both water and chloride O/I values for the eleven studied catchments are summarized in Table 3. Water O/I values are below 0.1 for 9 of the 11 catchments, with two exceptions. The ratio is 0.32 for Onkaparinga catchment (7 in Table 3) with the stream gauge at Houlgrave. This high value is apparently a result of Murray-River water input at an upstream location. Consistently, chloride O/I has a value of 7.1. Based on our definitions in Fig. 1, this is likely a type III catchment, further evidence will be given later. Another exception is North Para River catchment (11 in Table 3) with stream gauge at Mt McKenzie. Water O/I value for this catchment is 0.23, with abnormally high chloride O/I value of 31.4. Monthly hydrograph and stream chloride concentration are shown in Fig. 5a. No cross-catchment surface water transfer exists for this area. Neither is other obvious industrial water effluent observed. This is consistent with the monthly hydrograph which shows peak flow occurring in raining seasons. It is likely that cross-catchment groundwater transfer occurs. The abnormally high chloride O/I value indicates a chloride disequilibrium condition. This is supported by large fluctuation of stream water chloride concentration. Chloride concentration ranges from below 200 mg/l during the event flow to close 4000 mg/l at the beginning of raining seasons. Thus, this catchment is possibly a combination of types VI and IV. Except for these two, six of the remaining nine catchments (1, 2, 4, 5, 6, and 10 in Table 3) have chloride O/I value ranging from 2 to 4. They are most likely type VI catchments. One type V example of hydrograph and stream chloride concentration is shown in Fig. 5b for Bremer catchment (1 in Table 3). Similar to North Para River catchment, it has a large stream water chloride concentration range (from 300 to 3700 mg/l), good evidence of a type VI catchment.

The remaining three catchments (3, 8 and 9 in Table 3) have chloride O/I values around 0.5. They can be either a type I, II, or V catchment. For catchment (3), it has a type VI sub-catchment (catchment 1 in Fig. 2), thus it should be in chloride disequilibrium. In other words, this is a type V catchment. Because historical soil chloride is not leached into the stream, stream chloride concentration in a type V catchment does not fluctuate as much as that in a type VI catchment. This is evident in the time series of monthly chloride concentration for catchment (3) in Fig. 5c, showing that stream water chloride concentration ranges from 300 mg/l to only about 800 mg/l. For catchment (8), hydrograph (Fig. 5d) shows that base flow persists throughout the year. It cannot be a type VI catchment based on the chloride O/I value. It is most likely a type II catchment. This is supported by a low stream chloride concentration range (slightly above 100 mg/l to about 400 mg/l). As base flow in dry seasons is so small, resulting in negligible chloride load from base flow in contrast to event flow chloride load (not shown), this catchment can be regarded as a type I catchment. This is supported by a low water O/I value (Table 3). For catchment (9), it is difficult to determine chloride equilibrium condition solely based on the chloride O/I value. The stream is ephemeral, only flowing three to four months during raining seasons. Chloride concentration in stream water is below 400 mg/l (not shown). Climate condition will be incorporated to determine its chloride equilibrium status, discussed in the next subsection.

4.2 Relation of chloride equilibrium status and precipitation

For the six type VI catchments (Table 3), correlation analysis between chloride O/I and climatic (precipitation), hydrological (water O/I, streamflow), and catchment geometric (area, elevation, and slope) variables are preformed, with the results summarized in Fig. 6. Among the six examined variables, only annual precipitation is significantly correlated to chloride O/I, with a Pearson correlation coefficient of 0.89. This correlation is statistically significant at a confidence level of 98% (p value=0.017). Based on this result, regression of chloride O/I values with annual precipitation for the six type VI catchments is performed (Fig. 7a). The regression result suggests that chloride O/I value decreases with annual precipitation, consistent with the conceptual model shown in Fig. 4. For comparison, plots of cumulative stream chloride load vs. cumulative streamflow are included in Fig. 7b, showing that stream chloride concentration, inferred from the slopes of the curves, generally decreases with annual precipitation for the six type VI catchments. With an assumption that a chloride O/I value of one indicates new chloride equilibrium condition, at present a catchment with annual precipitation of 960 mm would have reached new equilibrium. As the forest clearance occurred in the MLR area 100–150 years ago, this regression result indicates that it takes less than 100–150 years for a catchment of 960 mm annual rainfall to reach new chloride equilibrium. This timing is consistent with what is found in the southern part of Murray-Darling Basin (Jolly et al., 2001), in which new salt equilibrium is estimated to reach within 100 years after forest clearance, for a catchment of annual rainfall above 900 mm.

The above results suggest that in the MLR area, a catchment of annual precipitation larger than 960 mm has already reached new chloride equilibrium by now (2008). A catchment of annual precipitation much smaller than 960 mm would still be at chloride disequilibrium. This is consistent with earlier discussion regarding chloride equilibrium status on catchments 1 (type VI, annual precipitation 574 mm), 2 (VI, 768 mm), 3 (V, 610 mm), 4 (VI, 802 mm), 5 (VI, 710 mm), 6 (VI, 610 mm), and 10 (VI, 813 mm) (Table 3). According to this annual precipitation threshold, Pedler Creek (catchment 9, annual precipitation 736 mm) is in chloride disequilibrium. It should be a type V catchment at present. As the threshold of 960 mm annual precipitation was derived from type VI catchments, it takes into account the time required to transport historical chloride in the vadose zone and in shallow groundwater into the stream. It is likely that a catchment with annual precipitation slightly below 960 mm has reached new equilibrium. Onkaparinga @ Hahndorf (catchment 8, precipitation 838 mm) can be such an example. Onkaparinga @ Houlgrave (catchment 7, precipitation 871 mm) should have reached new chloride equilibrium, supporting earlier discussion that it is a type III catchment. In summary, a catchment of annual precipitation around 900 mm most likely has reached new chloride equilibrium in the MLR area.

4.3 CMB method estimated groundwater recharge

Of eleven examined catchments, two are most likely in new chloride equilibrium, and valid for CMB application. They are catchments 7 and 8, of which catchment 7 receives Murray River water. To avoid the complexity due to cross-catchment water input, CMB estimation is only performed for catchment 8. As most groundwater samples over this catchment (Fig. 2) are depth average samples, it is not appropriate to be used as the recent recharge groundwater for CMB calculation. With an assumption that chloride concentration is larger over the non-equilibrium period, catchment-average currently recharged groundwater chloride concentration is estimated from the left end of the histogram of all available samples (Fig. 8). A range of 25 to 125 mg/l is used for Eq. (2), resulted in a net groundwater recharge rate of from 20 to 90 mm/year for this catchment, about 2 to 12% of annual precipitation. If a value of 75 mg/l is used for chloride concentration of average currently recharged groundwater, the net groundwater recharge is estimated to be 30 mm/year, about 4% of annual precipitation. Please note that this estimate is the net groundwater recharge from the catchment. It is smaller than the vertical water table recharge which is based on point chloride balance. It is worth to emphasize that net catchment groundwater recharge, instead of direct water-table recharge, should be used for groundwater resource allocation.

5 Conclusions

To examine CMB applicability for groundwater recharge estimates in the MLR, an area having experienced widespread historical vegetation clearance, catchment chloride budget was investigated based on a recently constructed atmospheric chloride deposition map. Six conceptual catchments of various chloride equilibrium statuses are defined, based on conditions that might happen in the MLR region. The conceptual models are examined with eleven selected catchments of various sizes and climate conditions. The results show that six of the eleven catchments match type VI chloride equilibrium condition (chloride disequilibrium with a gaining stream), with catchment chloride O/I values ranging from 2 to 4. Two catchments match type V chloride equilibrium condition (chloride disequilibrium with a losing stream), with catchment chloride O/I values about 0.5. For these catchments, the CMB method is not appropriate to apply. The results also suggest that neither a below-one chloride O/I value nor a low fluctuation of streamflow chloride concentration (a factor below 4) guarantees a chloride equilibrium condition. But a large chloride O/I value (above one) and a large fluctuation of streamflow chloride fluctuation (a factor of 10 and above) generally indicates either a chloride disequilibrium or cross-catchment water transfer, or both, for which CMB is not applicable. Based on the regression between type VI catchment chloride O/I values and annual precipitation, a catchment with annual precipitation around 900 mm in the MLR has most likely reached new chloride equilibrium, for which CMB can be applied given that no cross-catchment water transfer occurs. CMB is applied for one catchment at chloride equilibrium, resulted in a net catchment groundwater recharge estimate of 30 mm, about 4% of annual precipitation.

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Table 1. Water and chloride ratios of five experimental catchments in (Williamson et al., 1987) and their corresponding chloride equilibrium types. The forest clearance occurred at the end of 1976.

	Catchment	Area (km^2)	Data period	Precipitation (mm)	Water O/I	Cl O/I	Type
Forested	Salmon	0.82	1974–1983	1123	0.11	1.37	II or IV
	Ernies	2.70	1974–1983	738	0.02	0.09	I
Cleared	Wights	0.94	1977–1983	1027	0.31	9.79	VI
	Dons	3.50	1977–1983	721	0.02	0.14	V
	Lemon	3.44	1977–1983	737	0.03	0.22	V

Table 2. Eleven selected catchments in the Mount Lofty Ranges and related site information.

Catchment	Gauge ID	Easting (m)	Northing (m)	Data-period[a]	Area (km2̂)	Elevation[b] (m)	Slope (degree)
1. Bremer @ U/S	4260688	320374	6110330	1998–2007	195	260 (67–534)	6
2. Western Flat Creek	4261018	303709	6116027	2005–2006	33	382 (317–472)	5
3. Bremer @ Bletchley	4261070	317686	6097406	2005–2008	604	252 (28–534)	6
4. Finniss River	4261075	297642	6089905	2005–2008	278	307 (102–481)	7
5. Currency Creek	4261099	296277	6074320	2007–2008	76	215 (15–400)	6
6. Giles Creek	4261103	300432	6085034	2007–2008	30	154 (30–372)	5
7. Onkaparinga @ Houlgrave	5030504	292589	6115458	2008/2009	334	412 (223–704)	7
8. Onkaparinga @ Hahndorf	5030537	298622	6122518	2003–2007	229	420 (295–615)	6
9. Pedler Creek	5030543	274330	6101476	2001–2005	85	164 (40–405)	6
10. Torrens River @ Mt Pleasant	5040512	319631	6148870	2006/2008	26	465 (413–543)	3
11. North Para River @ Mt McKenzie	5050533	323834	6172797	1997–2007	44	440 (364–584)	4

[a] 1998–2007 indicates whole-year record from 1998 to 2007 (inclusive), and 2006/2008 indicates part-year record for the two end years.

[b] This is elevation calculated from 25 m-DEM, with the first number being average elevation above sea level, and the two numbers in the brackets being the elevation range of the catchment.

Table 3. Atmospheric input and streamflow output of water and chloride of the eleven catchments and their possible corresponding chloride equilibrium status.

Catchments	Gauge ID	Precipitation (mm)	Streamflow (mm)	Water O/I	Cl deposition (g/m^2)	Stream Cl load (g/m^2)	Cl O/I	Chloride equilibrium types
1. Bremer @ U/S	4260688	574	16	0.03	3.7	14.9	4.1	VI
2. Western Flat Creek	4261018	768	22	0.03	4.3	9.8	2.3	VI
3. Bremer @ Bletchley	4261070	610	5	0.01	4.1	2.2	0.5	V
4. Finniss River	4261075	802	61	0.08	5.2	11.2	2.2	VI
5. Currency Creek	4261099	710	59	0.08	6.1	21.3	3.5	VI
6. Giles Creek	4261103	607	27	0.04	5.5	17.2	3.1	VI
7. Onkaparinga @ Houlgrave	5030504	871	279	0.32	4.4	30.9	7.1	III
8. Onkaparinga @ Hahndorf	5030537	838	8	0.01	4.2	1.9	0.5	I or II
9. Pedler Creek	5030543	736	16	0.02	5.0	2.2	0.4	IV
10. Torrens River @ Mt Pleasant	5040512	813	8	0.01	3.2	6.4	2.0	VI
11. North Para River @ Mt McKenzie	5050533	723	168	0.23	3.1	97.7	31.4	IV and VI

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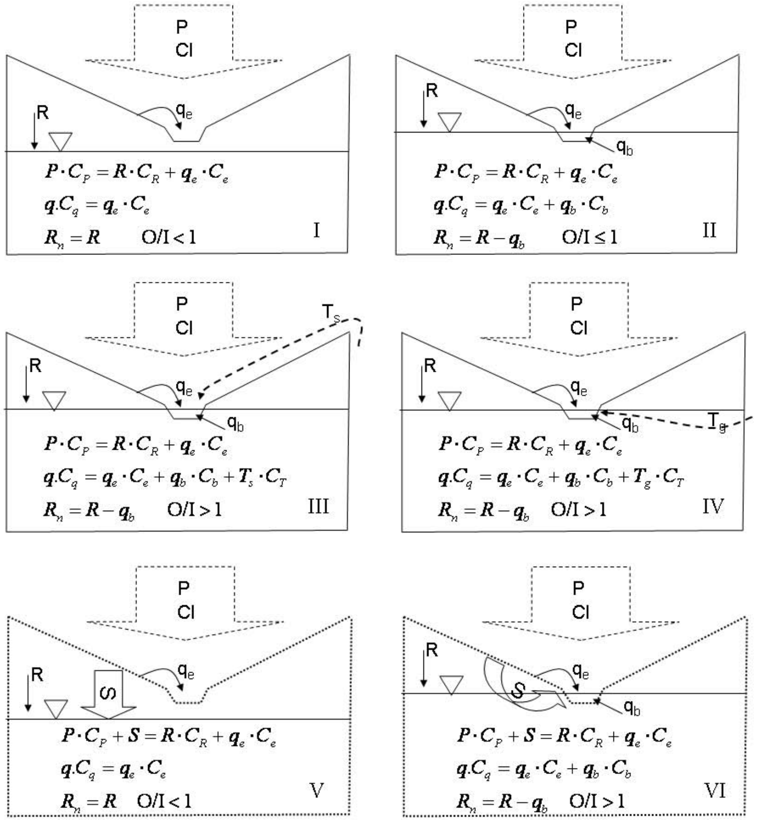

Fig. 1. Conceptualization of catchment chloride balance under various conditions: (I) Chloride steady state with a losing stream, (II) Chloride steady state with a gaining stream, (III) Chloride steady state, with cross-catchment surface water transfer, (IV) Chloride steady state, with cross-catchment subsurface water transfer, (V) Chloride non-steady state, in which historical soil chloride is primarily leached to groundwater, and (VI) Chloride non-steady state, in which historical soil chloride is leached to both surface water and groundwater. The symbol meaning is P for precipitation, R for direct groundwater recharge, q_e for event streamflow, q_b for base flow from direct-recharge groundwater, T for cross-catchment water transfer, R_n for net groundwater recharge; all are average values in a unit of mm evaluated over the whole catchment. And Cl is for chloride deposition in mg/m^2, Cis chloride concentration (unit: mg/l) of various water flux indicated by the subscript, in which C_p (=Cl/P) is the bulk precipitation chloride concentration. S is the re-mobile historical soil chloride leached into the stream and groundwater, in a unit of mg/m^2 over the whole catchment. O and I denote chloride being exported out of the catchment via streamflow measured at the outlet point, and chloride input from atmospheric deposition to the catchment, respectively.

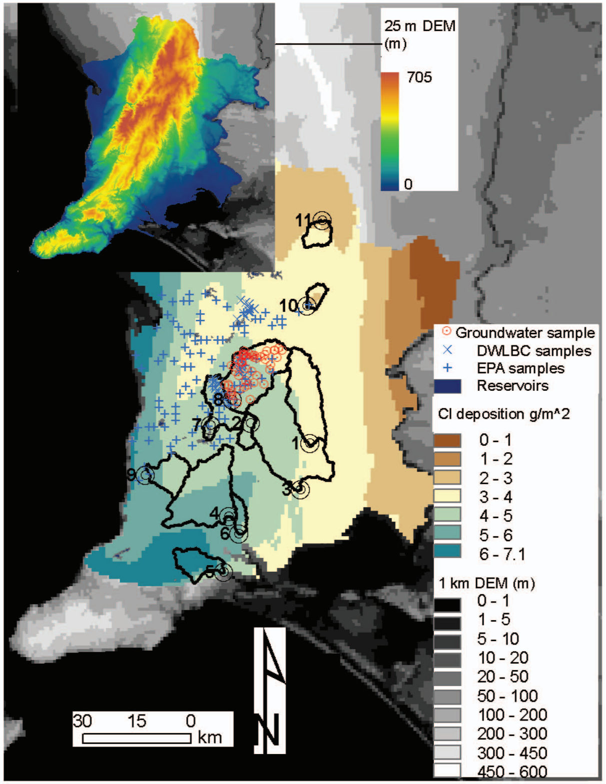

Fig. 2. Eleven catchments (the numbers matches those in Table 2), overlaying the annual chloride deposition map (Guan et al., 2009a), with distributed DWLBC and EPA stream water samples used to derive the relationship between chloride concentration and EC measurements, and groundwater samples of chloride concentration for CMB application. The insert map is 25-m DEM of the MLR area. Note that catchment 7 includes catchment 8, and catchment 3 includes catchment 1. The river in the east, flowing to the south, is Murray River, which provides about 50% of water for the Adelaide metropolitan area via three main pipe lines (not shown).

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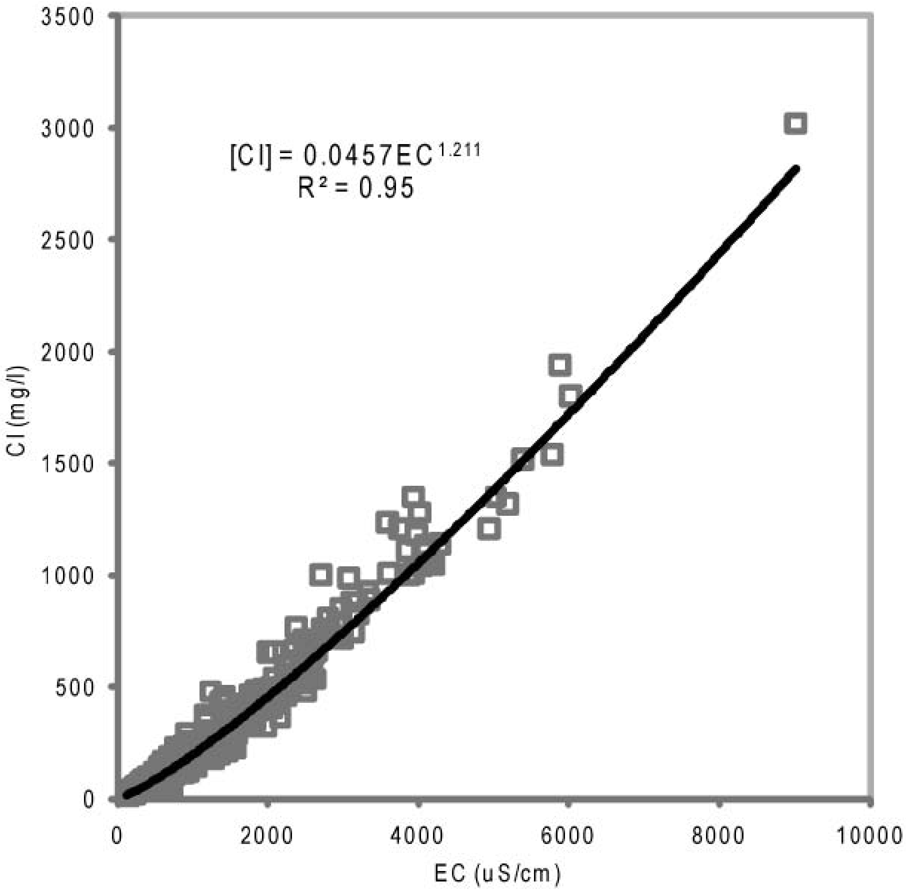

Fig. 3. Measured chloride concentration of stream water vs. measured electrical conductivity values, based on 306 samples by EPA mainly collected in May and October, and 145 samples by DWLBC collected in November, December, March, and July.

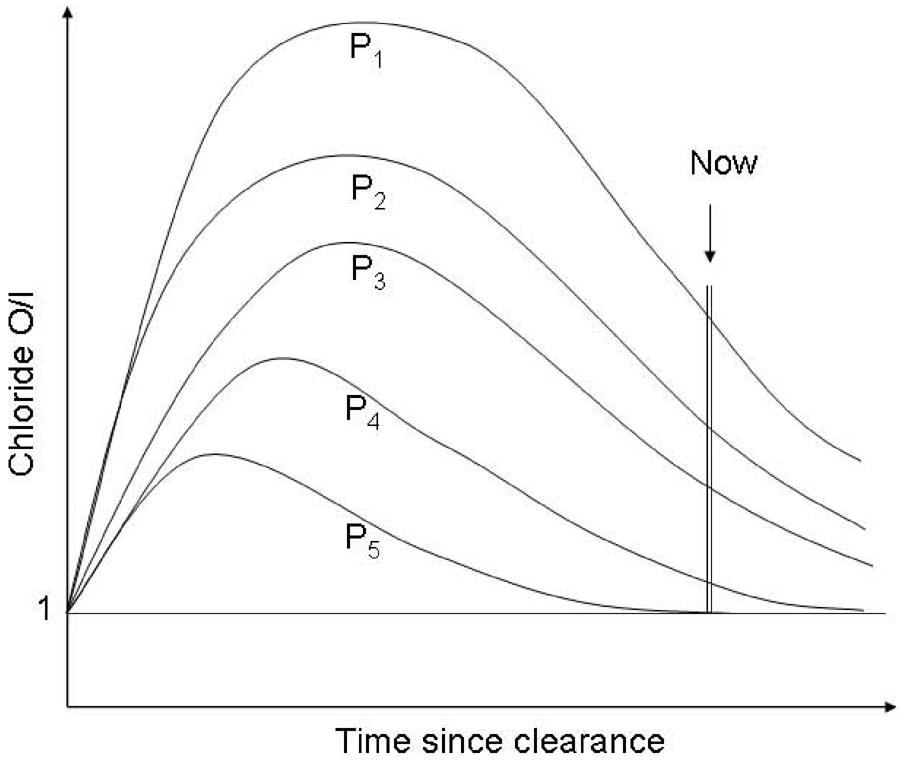

Fig. 4. Conceptualized evolution paths of type VI catchments starting from the forest clearance to type II catchments as a function of climate conditions, where precipitation increases from P_1 to P_5, (extended from Fig. 2 in Jolly et al., 2001).

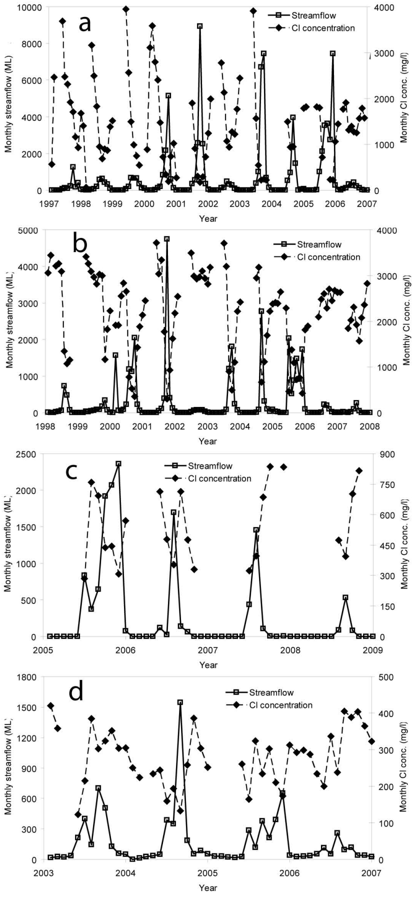

Fig. 5. Monthly series of streamflow and water-weighted average monthly chloride concentration in stream water for four selected catchments: **(a)** North Para River catchment with gauge ID 5050533, **(b)** Bremer catchment with gauge ID 4260688, **(c)** Bremer catchment with gauge ID 4261070, and **(d)** Onkaparinga @ Hahndorf catchment with gauge ID 5030537.

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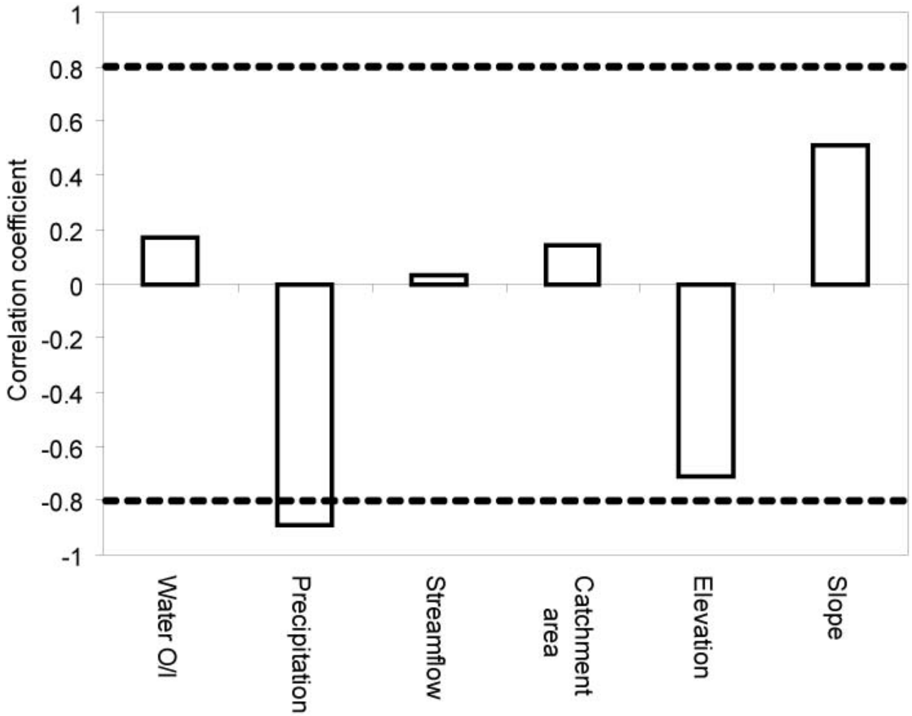

Fig. 6. Pearson correlation coefficient between chloride O/I and each of the six selected climate and catchment variables for six type VI catchments (Table 3). The dash lines are statistically significant linear correlation at 95% confidence level, showing that only precipitation is significantly correlated to chloride O/I values.

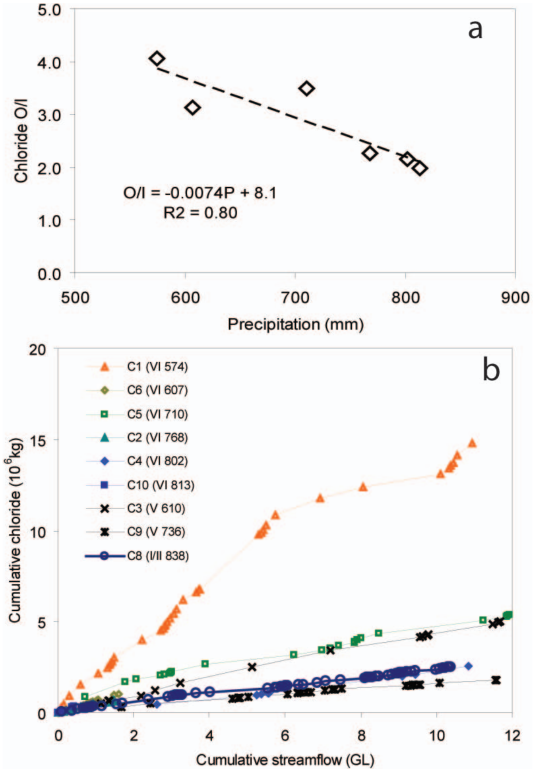

Fig. 7. **(a)** Catchment chloride ratio vs. catchment average annual precipitation for six type VI catchments, indicating that a catchment of an average precipitation of 960 mm would have now (2008) reached the new chloride equilibrium (type II). **(b)** Cumulative chloride load in the stream water vs. cumulative streamflow for six type VI catchments, showing that the average chloride concentration (the slope of the curve) decreases with increasing annual precipitation (the number in the legend), with two type V catchments and one chloride equilibrium catchment for comparison.

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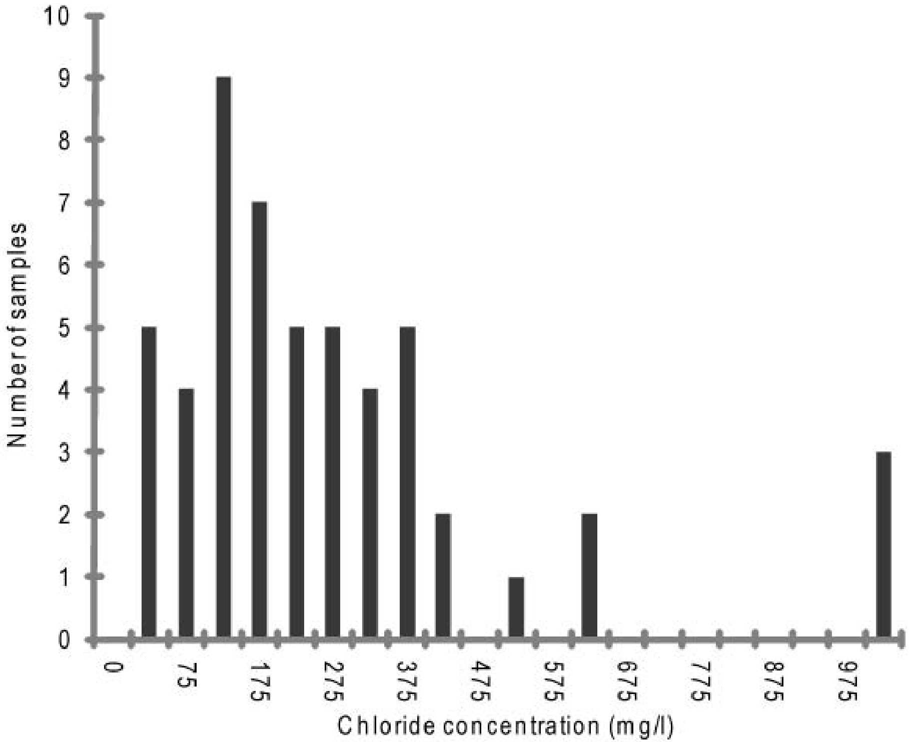

Fig. 8. Histogram of chloride concentration from 52 groundwater samples collected at various depths in the catchment 8.