Response to the reviewers' comments (2) on HESS-2009-213

Dear Dr. Crosbie,

Your comments and suggestion on the manuscript are appreciated. Below are our responses. Look forward to your further suggestion.

Sincerely,

Huade Guan
On behalf of the co-authors.

General comments

(1) This manuscript investigates a worthwhile topic in the mis-use of the chloride mass balance (CMB) method of estimating recharge. This is a very well used technique that could be used inappropriately if the inherent assumptions are not adhered to.
The central idea in this manuscript is that output-input ratios of chloride can be used as a method of determining if a catchment has reached equilibrium after a land-use change. If it has not reached equilibrium the authors assert that the CMB cannot be used. There are many problems with this idea. The most obvious being that no justification is given to why O/I ratios are useful, if part of the source of chloride is geochemical rather than entirely cyclic then equilibrium will never occur. Not being able to use the CMB when the catchment is not in equilibrium is wrong. Methods have been developed over the decades that account for non-equilibrium and are used routinely – there is no mention within the manuscript of these techniques (Allison and Hughes, 1978; Walker et al., 1991).

Discussion
(On O/I ratio)

Chloride is widely used as a conservative environmental tracer. The primarily source is from atmospheric deposition. Geochemical source (from rocks) chloride occurs only from some evaporative rocks. For most of the rock types, such as granite, limestone, and metamorphic rocks, the contribution of chloride from the rock is negligible in comparison to that from atmospheric deposition. Based on this, numerous CMB applications for groundwater recharge have been performed. In our study area, the bedrock is primarily late Precambrian metamorphous sedimentary rock composed of shale and sandstone, and some limestone (Preiss, 1987). We assume the geological source of chloride is negligible. Based on similar assumption, White et al., (2009) recently use chloride as reference to evaluate geochemical sources of other ions over the whole Murray-Darling basin, an area much larger than our study area.

Catchment chloride (or salt) O/I has been shown, used, or considered to be useful, to indicate forest clearance impact on catchment chloride equilibrium status (Peck and Hurle 1973, Williamson et al., 1987, Cook et al., 1989,Williamson and van der Wel 1991, Jolly et al., 2001, Peck and Hatton 2003). Based on these previous studies (most of them were cited), we proposed to use chloride O/I ratio, in corporation with other information, to estimate whether chloride has reached new equilibrium after forest clearance. Please also, note that we don't use this ratio as an absolute criterion.

(On chloride equilibrium for CMB application)

We would not count the techniques based on chloride front displacement (Allison and Hughes, 1978; Walker et al., 1991) as CMB. The CMB should be based on the formula , chloride input = chloride output, without a change in storage. The chloride equilibrium condition gurrantee that the storage change term is zero.
When chloride-based method is applied in vadose zone, both CMB (more common) and chloride front displacement (less common) methods have been used. The CMB method has been used in some profiles with climate/vegetation changes only when the chloride profile of the old steady state has not been disturbed (such as in Philips 1994). When chloride based method is applied in saturated zone, only CMB can be used.

Action

Apparently, we have oversimplified the above points in the manuscript, which will be elaborated in the revision.

(2) Being able to predict the time taken to reach equilibrium after a land use change is something that would be useful to know. There is a history of literature on this subject due to research into dryland salinity that has been ignored by this manuscript (Dawes et al., 2004; Gilfedder et al., 2003). If this literature had been read, then the authors could have tested if the hydrogeological properties of catchments, which theory tells us are relevant to the time required for equilibrium, rather than the hydrological properties tested that were not relevant for the time required to reach equilibrium. As the manuscript is presented I cannot recommend it for publication.

Discussion

We agree that hydrogeological parameters (such as hydraulic conductivity) and variables (such as of depth to water table) influence the time to reach new equilibrium. But we don't agree the hydrological conditions (especially the climate) are not important. Instead, over the small study area (9000 km^2), with a strong climate gradient (precipitation ranges above 1000 mm to below 500 mm), we believe climate factors are very important. Similar conclusion is made by Jolly et al., (2001) for the Murray-Darling Basin. (This reference was cited, but for some reason it was missing in the reference list of the manuscript. We apologize for this carelessness). Even in Dawes et al, 2004, precipitation is regarded as an important factor. The soil type is another important factor considered in Dawes et al. model. As soil properties vary a lot within any one of the catchments in our area, it is difficult to assign a value to each of the 12 catchment. Nonetheless, if we consider the controlling factor in soil formation: climate, topography, biotic factor (strongly related to climate), and parent material (including geology) (Birkeland 1999), three of the four major factors are related to surface conditions. Thus, we use readily available climate, topographic factor in our analysis.

Apparently, we have not made this clear enough in the manuscript.

Action

Some of the above text will be included in the revision, to justify our methodology.

Specific comments

(1) P7027, L19 The most important assumption in the CMB and the O/I ratios used here is that chloride is cyclic and sourced from precipitation. No mention has been made of this assumption or any justification for using O/I ratios in the case study. Rock weathering or other geochemical sources can be a source of chloride (Acworth and Jankowski, 2001).

Discussion and action
Please check our response to your general comment (1). This assumption will be mentioned with some support in the revision.

(2) P7027, L20 I am not sure that the CMB requires that recharge be constant. Recharge is dependant upon rainfall (amongst other things) so cannot be considered constant. Especially in semi-arid/arid areas where recharge is likely to be episodic. The CMB provides an average rate of recharge usually over the residence time of the water in the aquifer.

Discussion and action
By saying constant, we mean the average recharge rate does not change over years. Interannual variability is not considered here. We agree that the terminology here is ambiguous. This will be fixed in the revision.

(3) P7027, L25 Significant land use changes are not limited to coastal Australia, the inland areas have also been cleared for agriculture.

Discussion and action
We agree to rephrase this although we don't think our statement causes a problem.

(4) P7028, L3 I don't think *large amount* of water resources is the appropriate term here considering the water restrictions that have been imposed over the past few years due to a lack of water resources.

Discussion and action
We agree to rephrase it in the revision.

(5) P7028, L6 No support is given to the assertion that the CMB is the first recharge method to be considered.

Discussion and action
Based on a review by Petheram et al. (2002), of total 76 recharge estimate studies using 12 techniques in Australia, the CMB accounts for 1/3. We, however, agree to rephrase this in the revision.

(6) L7028, L25 There may not be a conceptual model specifically of chloride equilibrium, but many conceptual models have been developed for dryland salinity that could easily be applied to a CMB. No reference or discussion is given here to the Groundwater Flow Systems concept (Coram, 1998; Coram et al., 2000; Walker et al., 2003) or the models that have previously been developed to predict how long it takes a catchment to return to hydrological equilibrium after a land use change (Dawes et al., 2004; Gilfedder et al., 2003; Smitt et al., 2003).

Discussion and action
We were not aware of these references. Most of them are local reports which are not included in common academic database (e.g., web of science), and they cannot be found from the citation tree of Jolly et al. (2001). Your reminder is greatly appreciated. After checking Coram 2000 and Walker 2003, we don't find that the conceptual catchment types in terms of chloride equilibrium have been discussed. If you are talking about general

hydrological processes, similar concepts have been discussed more widely in the international literature. We believe the novelty in our manuscript is that we put relevant hydrological processes together in such a way to examine catchment chloride equilibrium status. Anyway, we agree to slightly rephrase our statement in the revision. The modeling effort on estimating the time for the system shift to new equilibrium will be included in the revision.

(7) P7029, L4 There should be 2 more classes in this classification. A catchment with a water transfer does not have to be in equilibrium with respect to chloride.

Discussion and action
We agree. Actually, we discuss in the results that catchment 11 can be both type IV and VI. We could add these two as you suggested. But even these two are added, we cannot exhaust the possibilities. For example, cross-catchment transfer can occur on top of type I (not necessarily of type II, as in type III and IV). Thus, we decide to use the six conceptual types, which have already very lengthy description. We add a sentence to explain the issue that you raised.

(8) P7030, L3 The CMB applied in the saturated zone does not estimate the amount of water that crosses the water table as is defined by R. It estimates the recharge (R) minus any evapotranspiration direct from the saturated zone (ET_{GW}) as phreatophytes will continue to concentrate the chloride after it has recharged the saturated zone. This quantity has been referred to as net recharge when using the CMB in Gnangara and Tomago. The use of net recharge in this manuscript is confusing considering the previous use of net recharge in studies using the CMB.

Discussion and action
The concept of net groundwater recharge has been used for a long time, which means the difference of recharge and discharge over the same area. One example we found is by Lawson 1971 (J of Hydrology (New Zealand)). The concept you mentioned is one contribution to reduce net groundwater recharge, in which the discharge occurs via water-table transpiration. But we agree that the contribution of water-table transpiration and base flow discharge, on groundwater chloride concentration, is different. We will clarify this in the revision, and discuss the phreatophyte effect as well.

(9) P7030, L5 Water resources should not be allocated on the basis of your net recharge. Any GW extraction from within the catchment will reduce baseflow, your net recharge changes with extraction. Some have even argued that recharge is irrelevant in water management and that it is discharge that should be focused upon (Bredehoeft, 2002).

Discussion and action
We agree that net groundwater recharge will change with the change of baseflow. This is why we use this concept in the framework, and quantitatively link to streamflow. Regarding the water resource management, the value of net groundwater recharge gives the amount of groundwater recharge from the examined catchment, with groundwater discharge to the steam excluded. We believe this would be more useful than the raw groundwater recharge without considering stream discharge, as baseflow can be very important to support biodiversity.

Another reason to use the concept of net groundwater recharge, is because of the difficulty to estimate direct water-table recharge (phreatophyte transpiration is included). As you point out later, we don't know how much precipitation becomes event flow, and how much chloride is included in the event flow.

(10) P7030, L10 How is $q_e.c_e$ to be determined? Event flow is complex mixture of overland flow, interflow and baseflow that is anything but simple to resolve (Hughes et al., 2008; Hughes et al., 2007).

Discussion and action
The two quantities are introduced for conceptual purpose. And we agree that they are complex. In some situation, they can be simplified. For example, in a type I catchment where based flow is missing, they are equal to stream flow and stream water chloride concentration, respectively.

(11) P7030, L14 Groundwater can discharge to the surface without becoming baseflow. This is the cause of dryland salinity and occurs in many catchments that have been cleared for agriculture.

Discussion and action
We agree. But this is not the case of a type I catchment. It is more likely to occur in a type VI (or maybe type V as well) catchment. We will discuss this situation with types V and VI catchments.

(12) P7030, L19 How do you determine that there is no change in the storage (S) of chloride in the unsaturated zone?

Discussion and action
In this conceptual type I, chloride is in equilibrium, which means no storage changes. Again, when we say in equilibrium, we mean that the mean condition of multiple years. We don't consider the effects of the climate variability (such as ENSO), or seasonality.

(13) P7030, L20 How can you be sure that all groundwater recharged within the catchment is discharged within the catchment? (Mitchell et al., 2006) describes a series of field studies that found local groundwater flow systems are far more complex than anticipated. At Boorowa most of the salt passed under the gauge (Crosbie et al., 2007) and at Brays Flat the groundwater flow direction was perpendicular to the stream network (Crosbie et al., 2008).

Discussion and action
No, we are not sure. A type II catchment allows that some discharge occur outside the catchment, as indicated in O/I <=1. We agree that the actually condition is complex. But this does not mean that we have to use complex method to tackle the problem. Anyway, we agree to mention the complexity when presenting our simple conceptual catchment types.

(14) P7031, L20 The CMB is estimating recharge not discharge. The O/I ratios are affected by water transfers, recharge is not. The CMB can be applied in a catchment with water transfers, it is the classification scheme proposed here that is not applicable in a catchment with water transfers. If the salt load is known that is exported/imported by water transfers then it can be accounted for in calculating the O/I ratios and then the system collapses back to a type I/II catchment.

Discussion and action

We agree. What you said was discussed P7031, L13-17. We will add some condition to L20 to clarify the issue.

(15) P7032, L4 The CMB can still be used in a catchment that has not reached equilibrium using modified forms. This has been done for decades. A steady state CMB can be performed in the unsaturated zone (Allison and Hughes, 1978) or if the unsaturated zone has not yet reached equilibrium then a transient CMB can be applied (Radford et al., 2009; Walker et al., 1991).

Discussion and action
Please refer to our response to your general comments. The main point is that the chloride front displacement method is different from the CMB. We will add a sentence to clarify this issue.

(16) P7033, L10 How do you know the catchment O/I ratios were in equilibrium prior to clearing?

Discussion and action
This is an assumption we made, based on that no abrupt climate change in the past several hundreds years has been reported, and that O/I ratio close to one is observed in many intact catchment. We will clearly state the assumption with supports in the revision.

(17) P7033, L25 Was one relationship between EC and Cl used irrespective of geology? Sandsone and Limestone will have quite differing relationships due to the presence of ions other than chloride.

Discussion and action
The waters flowing through different geological area may have different ionic composition, and thus may influence the relationship between [Cl] and EC. However, it is very difficult to derive separate relationship for different geological area. The total 450 stream-water samples cover the area with various bedrocks (metamorphous shale and sandstone, and carbonate rocks). As in the mountainous catchment, the average time of streamwater in contact with beckrock in its flow history is very short, the bedrock effect should be very small. We decide to use a mean relationship drive from all 450 samples for the whole area. Similarly, White et al. (2009) recently use one [Cl] – EC relationship for the whole Murray River and its tributaries, in an area which is much larger than our study area.

(18) P7034, L14 It should be noted here that the outputs calculated are surface water outputs and not groundwater outputs.

Discussion and action
We agree, and will make it clear.

(19) P7034, L14 The annual average streamflow and chloride load are based on very short time series during a drought. The most recent decade has not been representative of the time since land clearing and so should not be used in this manner (CSIRO, 2008).

Discussion and action
Over a similar area that the issue is discussed in CSIRO 2008, Murphy and Timball (2008) shows that the drought in recent years is not much different from the 50-year average before 1950.

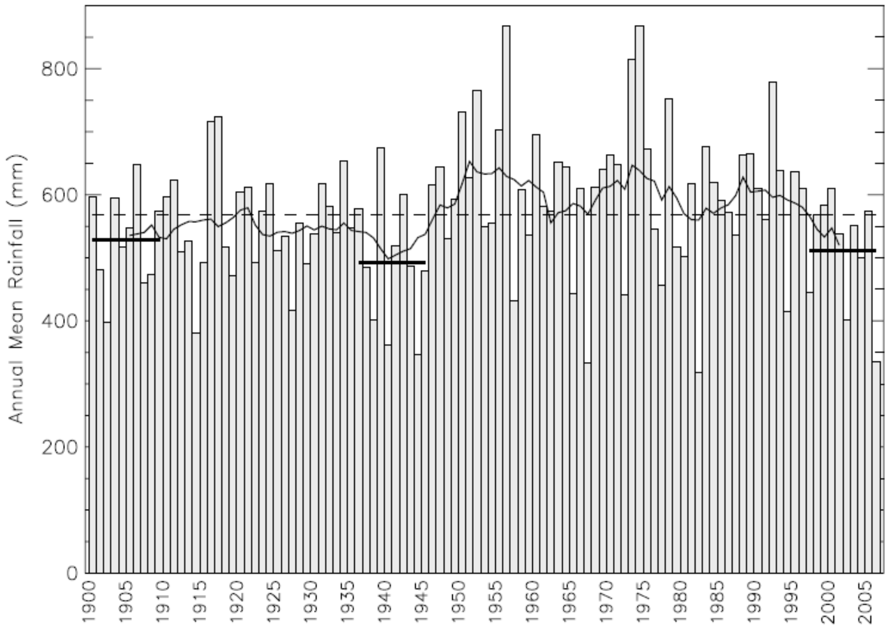

Figure 3. Mean annual rainfall over the southeastern Australia region (mainland south of 33 °S, east of 135 °E) for each year from 1900 to 2006. Also shown are the 1900–2006 mean (dashed line), the 10-year means for 1997–2006, 1900–1909 and 1936–1945 (thick, short horizontal lines) and the 11-year running mean (solid black). Units are in mm.

According to Bureau of Meteorology, in South Australia, the annual precipitation anomaly between 1997-2008 (the data period of this study) is -1.4 mm. For the most recent four years (2005-2008), the annual precipitation anomaly is -37 mm.

It would be nice to have data of a longer period, but it is not available. Based on the following points, we argue that it is acceptable to examine our conceptual models with the existing data.

- Drought may strongly reduce streamflow, but it does not reduce chloride load in the stream to the same degree. The stream water in drought years has higher concentration.
- Smaller fluctuation in precipitation may be dampened by vegetation, leading to smaller change groundwater recharge than the precipitation itself. This phenomenon is evident in Sandvig and Philips (2006).
- We examine the catchment chloride equilibrium status based on type VI catchments at the examined period. As long as historical chloride in the soil profile is released to the stream, it can be identified from the O/I ratio significantly exceeding 1.

Nonetheless, we agree that this is an issue and should be brought to readers' attention. In the revision, we will present the time-series of precipitation in the study area, and discuss the uncertainty that may cause.

(20) P7035, L6 No reference is given to how much of the native vegetation in the catchments have been cleared. I would expect different results if 20% has been cleared compared to 80% cleared.

Discussion and action

It is difficult to recover the exact vegetation clearing history. Based on information provided on http://www.environment.gov.au/, only 10% of original native vegetation is now left in the

Mount Lofty Range. It is estimated that a large portion of native vegetation has been cleared before 1900, some additional vegetation clearance occurs prior to the introduction of clearance controls in May 1983. The 10% of intact native vegetation is mostly concentrated near the Peak of Mount Lofty within catchment 7. The native vegetation in other examined catchments is very little. With this situation, we assume that they have similar vegetation clearance history. We have not discussed these details in the manuscript, which will be included in the revision.
About the different portion of vegetation clearance, its impact on catchment O/I ratio should be different. However, in terms of the time length to move to new catchment equilibrium, it is hard to estimate. If the vadose zone process (under similar climate) controls the journey back to new equilibrium, a catchment of 20% vegetation clearance may need similar time to reach new equilibrium as that for a catchment of 80% vegetation clearance.

(21) P7037, L19 Why not test any hydrogeological parameters? This paper is concerned with the groundwater coming into equilibrium. Previous approaches have shown that it is transmissivity, specific yield, recharge, length and head that determines how long it takes a catchment to reach equilibrium after a land use change (Gilfedder et al., 2003; Smitt et al., 2003).

Discussion and action
Please check our response to your general comment (2). We are not consider the whole aquifer is in equilibrium with new surface condition, but the vadose zone chloride and the top of groundwater that feed base flow to the stream. For the geological parameters, it is extremely difficult to get the data in our study area, where fractured rock aquifers are typical. The results from our simple approach are consistent with Jolly et al., 2001, suggesting that the factor we chose is significant and appropriate.

(22) P7037, L21 Is precipitation significant because it is a surrogate for recharge?

Discussion and action
Precipitation provides water for recharge. Larger precipitation leads to a larger drainage, and shorten the time for the system to move toward a new equilibrium.

(23) P7039, L7 You have gone to great length to explain that this particular catchment is at equilibrium and can be used to estimate recharge using the CMB, and then said that only the low end of the distribution of chloride in groundwater can be used because the high chloride is due to non-equilibrium conditions. This is not consistent, either the CMB can be used or it can't be used.

Discussion and action
This is because groundwater samples were collected over various ranges of screen-length. Chloride concentrations in these groundwater samples are average historically recharged water. It is not appropriated to use these old waters for calculating groundwater recharge at the new equilibrium (refer to our response to your comment 21). With assumption that the newly recharged water at the new equilibrium has a lowest chloride concentration, we chose the lower-end of the groundwater concentration distribution for CMB calculation. We will make this assumption clear in the revision.

(24) P7039, L10 The use of this range of values is very subjective and perhaps even arbitrary. (Eriksson, 1985) showed that the distribution of chloride in groundwater should be log-normally distributed and then argued that a harmonic mean should be used. Why is not appropriate to use a harmonic mean (or geometric mean) rather than select some number from the low end of the distribution?

Discussion and action
Please refer to our response to your comment (23).

(25) P7039, L10 How is $q_e.C_e$ determined? Event flow is complex mixture of overland flow, interflow and baseflow that is anything but simple to resolve (Hughes et al., 2008; Hughes et al., 2007).

Discussion and action
We calculate net recharge based on Eq. (2). The quantity of qe and Ce are not needed. Please check P7030 L26 - P7031 L1.

(26) P7039, L14 No account of the uncertainty is given for this recharge estimate? There is considerable uncertainty in the chloride deposition and chloride concentration of the groundwater, this uncertainty can be incorporated into the recharge estimate (Crosbie et al., 2009).

Discussion and action
Based on our mapping results, the uncertainty in the chloride deposition is about 20%. We will calculate the uncertainty in groundwater estimates from this source, and discuss the uncertainty from groundwater chloride concentration, which we cannot quantify.

(27) P7039, L17 This statement is wrong and should be deleted. Any extraction in the catchment reduces baseflow and therefore changes your net recharge number. But does not change your recharge number.

Discussion and action
We will rephrase this sentence, as in our response to your comment (9).

(28) P7046, fig 1 What about catchments that are gaining in one season and losing in another?

Discussion and action
We are looking at mean condition over a time scale of years. We will make this clear at the beginning in the revision.

(29) P7047, fig 2 The greyscale DEM cannot be seen behind the colour Cl deposition map. 2 figs perhaps?

Discussion and action
Thanks for the suggestion. We will improve the figure.

(30) P7053, fig 8 Are these 52 samples from the one bore? Or one sample from 52 bores? Or somewhere in between?

Discussion and action
It is based on 52 bores. The bore-hole locations are shown in Figure 2. We will make it clear here.

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