Author Reply to Prof. Warren Wood:

Theory of the generalized chloride mass balance method for recharge estimation in groundwater basins characterised by point and diffuse recharge

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The authors would like to thank Prof. Warren Wood for participating the discussion forum and for comments. The corresponding replies are listed as follows:

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Prof. Wood –C1: My concern with this analysis is the lack of recognition of the boundary conditions associated with the CMB (chloride mass balance) method (see Wood 1999 for their definition).

Author Reply: We recognise the importance of applying the correct boundary conditions. We consider the above comment is due to a slight oversight. Therefore, the assumptions and boundary conditions used are summarised below with the boundary condition of Wood (1999) for comparison. The later part of the Prof. Wood's comments (see **C5** below), it is acknowledged that authors have used all assumptions in Wood (1999). It is stated that *"….which require basically the same assumptions as the CMB*", somewhat contradicts the statement in **C1** above.

We have not specifically mentioned the boundary conditions stated in Wood (1999) in this manuscript as they are given in the revised manuscript of doi:10.5194/hessd-10-11423-2013 (Hydrological functions of sinkholes.., which is currently under review).The fundamental basis of the conventional CMB method is that recharge mass flux crossing the watertable plane can be calculated if the following conditions are met (Wood 1999, Gee et al. 2005):

- chloride in the groundwater originates from precipitation directly on the aquifer, and no unmeasured runoff occurs;
- there is a steady influx of water and chloride; and
- chloride is conservative in the system and there are no other sources or sink in the aquifer,

Wood (1999) states that :

"*If these conditions (*the assumptions and boundary conditions given above*) are met, then the areally averaged recharge flux to the aquifer can be expressed as a simple linear relationship:*

$$q = \frac{(P)(Cl_p)}{Cl_{gw}} \qquad (1)$$

Where q is the groundwater recharge flux (LT^{-1}), P is the average annual precipitation (LT^{-1}), Cl_p is the average precipitation-weigthed chloride concentration (ML^{-3}), and Cl_{gw} is the average chloride concentration in the groundwater (ML^{-3}). M is mass, T is time, and L is length in consistent units."

Because in our manuscript we are deriving a generalized approach to extend the chloride mass balance method to include point sources (by pass flow), we have applied the law of conservation of mass at three levels, at the ground surface, and in the unsaturated and saturated zones. At each level, relevant boundary conditions were applied and those include the Wood (1999) boundary conditions (as Prof. Wood admitted in **C-5** below-highlighted). Please see below, boundary conditions and assumptions used in the derivation of the Generalized CMB.

At the ground surface level (page 316, Lines 20-24):

- The storage fluctuation term is assumed to be negligible, if the time of integration is sufficiently long to cover several hydrological years.
- Water is assumed to evaporate in its pure form and therefore no chloride is lost through evaporative fluxes.
- It is assumed that chloride concentration in surface runoff contributing to point recharge and in infiltrating water remain the same.

At the unsaturated zone the assumptions and boundary conditions are (page 317, Lines 3-9):

- The upper boundary of the unsaturated zone is taken to be the ground surface with infiltration rate F, and the lower boundary of the unsaturated zone is taken to be the watertable with recharge rate, R_u.
- The unsaturated zone storage fluctuation term may then be assumed to be negligible if the time of integration is selected to be long enough to cover several hydrological years.
- Loss of chloride by transpiration from unsaturated zone is negligible.
- The catchment is not subject to major land use changes.

Saturated zone assumptions and boundary conditions are (page page 317, Lines 20 – page 318, Line 3):

- The upper boundary is the watertable plane where the point and diffuse recharge enter the saturated zone and the lower boundary is the impermeable base.
- Groundwater chloride in the saturated zone is derived only from recharge.
- There is no chloride loss from the saturated zone through evapotranspiration.
- Lateral fluxes, upward and downward leakage do not result in changes in chloride concentration.
- There is no irrigation recycling or waste water irrigation input.
- In diffuse recharge, recharging water chloride is in equilibrium with groundwater chloride and therefore is equal to groundwater chloride concentration (c_u=c_{gd}).

Thus the boundary conditions of Wood (1999) are not ignored but some assumptions have been added ('no land use changes etc').

Prof. Wood –C2: That is, the authors claim that the CMB method is inappropriate in aquifers exhibiting variable spatial recharge rates. The authors are certainly correct in their assessment of the large hydraulic heterogeneity of karst systems; however, they appear to have confused the physics of the mass balance approach with the sampling problems associated with heterogeneity.

Author Reply: We thank Prof. Wood for this comment as it highlights that our description requires clarification.

The problem associated with the application of the conventional CMB (Equation (1) above and in Wood (1999)) to groundwater basins with point recharge is twofold (1) physics of the mass balance approach and (2) representative sampling problems. The physics of the mass balance approach is provided below and the sampling problem is described in **C3**.

Firstly, some key assumptions behind Equation (1) do not apply when point recharge is a contributing factor. This is explained further by rearranging Equation (1) as: $q\ (Cl)_{gw} = P\ (Cl)_p$. Note that q is the water mass flux crossing the watertable plane (Wood, 1999), or recharge. Under resident-type conditions, q should have the chloride concentration of the lower part of the unsaturated zone (Cl_{uz}). For convenience, Cl_{uz}, is replaced with Cl_{gw} , and note that they are equal only when the recharge flux is derived from diffuse recharge where chloride in recharging water [$(Cl)_{uz}$ in Wood, 1999] is in equilibrium with groundwater chloride, $(Cl)_{gw}$. Under this condition, the mass balance equation can be applied to clouds/rain [$P\ (Cl)_p$] and the watertable [$q\ (Cl)_{gw}$] to get Equation (1) assuming no chloride mass loss in between.

When point recharge is present, recharge fluxes crossing the watertable plane come from two streams (diffuse and point recharge) with two different chloride concentrations (c_s and c_{gd} or Cl_{uz}) which are often not in equilibrium with ground water chloride $(Cl)_{gw}$. Without such equilibrium, the chloride mass balance : $q\ (Cl)_{gw} = P\ (Cl)_p$ cannot be applied to clouds/rain and watertable [Note that the generalized CMB is equal to the conventional CMB equation given in Eq. (1), **when point recharge is equal to zero (Q_p =0)** (see Eq. 13a in page 319)]. When point recharge is present we use the generalized form of the CMB to account for this extreme flux-type condition.

Of course, there is an area of uncertainty if the two streams (point recharge and diffuse recharge) mix well before arriving at the watertable, OR mix well in the watertable. If this happens no distinguishable point or diffuse recharge crosses the watertable plane. Therefore, the recharge flux arriving at the watertable plane may have the chloride concentration as in saturated zone (at least approximately) and the conventional CMB is still applicable. This may apply to the case of point recharge through root channels, burrows, cracks and minor fissures or in large regional aquifers, such as the case reported by Herczeg et al (2003) where point recharge is 10% of the total recharge in the regional Tatiara catchment (>500 km^2).

Prof. Wood –C3: For example, if one had a steady-state chemically homogeneous and isotropic aquifer with no sources of chloride other than precipitation and had a constant spatial and temporal value of chloride in the precipitation, a single groundwater sample would suffice to estimate regional recharge of the entire aquifer. If the aquifer were heterogeneous containing areas of both focused and diffuse recharge, then a single sample is unlikely to represent the average value. Thus, groundwater-sampling density in a heterogeneous system is critical in acquiring an unbiased estimate of the average chloride concentration, thus, average recharge flux.

Author Reply: We agree that increasing groundwater sampling density can reduce uncertainties concerning spatial and temporal variability of recharge. If the aquifer is heterogeneous containing areas of both focused (point) and diffuse recharge, then there are difficulties in obtaining an average groundwater chloride measure and in applicability of the conventional CMB as described below.

1. When groundwater compartment (mixing) occurs, it is not possible to obtain representative samples due to a wide spectrum of chloride values that are possible between two end members; that is chloride associated with point recharge and ambient groundwater in the plume. This is similar to Aquifer Storage and Recovery (ASR) wells, where different concentrations of groundwater chloride exist, radiating from the point of recharge location outwards to ambient groundwater chloride concentrations. This is true no matter how small or large the volume of point recharge is. For example in Fig. 4 (see page 331), groundwater chloride for a drainage well (which is point recharge source) is (21.1 ± 21.6 mg/L) and for a monitoring well, (which is a sampling point) is (63 ±26 mg/L). In the Poocher Swamp fresh water lens, the surface water chloride concentration is 28 mg/L in the Swamp, 40 mg/L in nearby wells, and outside the lens in the diffuse recharge zone the chloride concentration is greater than 550 mg/L. When such extreme variation in groundwater chloride occurs due to extreme point recharge, the very definition of 'representative samples' becomes questionable. Even if one increased the sampling density, in the hope of getting average chloride values, it could still grossly underestimate the recharge.

   In our three case studies, the point recharge flux is estimated to contribute 63%, 85% and 98% of the total recharge for Uley South, Mount Gambier and Poocher Swamp fresh water lens respectively. This is greater than the point recharge contribution to regional aquifer reported by Herczeg et al (2003) but is similar to observations reported by Wood et al (1997).

2. Consider three cases of fully mixed aquifers. (a) receives only diffuse recharge (b) receives only point recharge (c) receives both diffuse and point recharge but imagine the aquifer is fully mixed (no fresh water pockets or plumes etc. and instantaneous mixing occurs between diffuse and point recharge).

   (a) In this case when rain water moves through the soil profile chloride enrichment takes place due to evapotranspiration and c_p enriches to Cl_{uz} and is in long-term equilibrium with Cl_{gw} (Wood, 1999). **Any variability in chloride concentration is due to variability in unsaturated zone properties, evapotranspiration and variability in rainfall etc, and can be accounted by taking basin average or weighted average chloride to get average recharge**. In this case Eq. 1 can be derived using the mass balance approach described in C2.1 above. This is also given by the generalized CMB in page 319, Eq. 13a when $Q_p = 0$.

   (b) In this case, total aquifer water/chloride is derived entirely from point recharge. Therefore, no chloride enrichment takes place due to evapotranspiration, and hence the aquifer water contains a chloride concentration that is equal to surface runoff chloride (c_s). In this case, recharge essentially takes place by bypass flow at discrete locations (sinkholes or drainage wells), and recharging water chloride (c_s) is equal to groundwater chloride ($c_g = c_s$) because surface runoff is the only source of chloride. As the chloride in recharging water crossing the watertable plane is in equilibrium with groundwater chloride, Eq. 1 is still applicable (this is derived from the generalized CMB by making diffuse recharge equal to zero and arrived at in Eq. 13b on page 319). **Any variability in chloride concentration is due to the spatial variability in rainfall and chloride concentrations, and different amounts of evaporation, if any, at different locations across the aquifer etc. Such variations can be assessed by taking basin average or weighted average chloride to get the average recharge**.

(c) This case is largely the point of contention. As we have pointed out above, the groundwater chloride concentration (C_{gw} in Wood, 1999) and c_g in this manuscript) lies between c_s and C_{uz} (in Wood, 1999; c_{gw} in this manuscript). We have expressed this in page 318, Line 7 as: $c_s \leq c_g \leq c_{gw}$. Note that at point recharge locations, we assume that recharging water or mass flux crossing the watertable plane is not in equilibrium with groundwater chloride because $c_s \leq c_g$. Similarly, at diffuse recharge locations, the chloride concentration of recharging water (or mass flux of water crossing the watertable plane) is not in equilibrium with groundwater chloride because $c_g \leq c_{gd}$ (C_{uz} in Wood, 1999).

(3) In real world situations, when the aquifer is not fully mixed there are difficulties in obtaining average representative chloride samples from heterogeneous (karstic aquifers). We have shown in an earlier manuscript, doi:10.5194/hessd-10-11423-2013 (Hydrological functions of sinkholes..), that it is not possible to measure representative samples due to the unknown extent of both the plume and the spread of conduits. We have shown using salinity profiles that low salinity freshly recharged water from point sources move at varying depths in the Blue Lake capture zone, Mount Gambier. We have cited an example from Herczeg et al (1997) in their study on Poocher Swamp sinkhole recharge. Herczeg et al (1997) established three monitoring wells at 10 m, 50 m and 150 m down-gradient of the two sinkholes to study the water level behaviour during recharge. The first two (shallow) wells terminated at 6 m below water level, and the third well (at 150 m) terminated at 50 m depth and about 35 m below the water level. The maximum water level rise was observed at the well 150 m from the sinkhole indicating a direct sub-surface connectivity to the sinkhole.

(4) An attractive feature of the generalized CMB equation is that it is not necessary measure groundwater chloride (c_g or Cl_{gw} in Wood, 1999) as it is not required in the equation. Instead generalized CMB uses only c_{gd} (OR C_{uz} in Wood, 1999) which can be obtained from soil water extraction described above or measuring diffuse zone chloride concentrations. Therefore, uncertainty associated with extreme variability of groundwater chloride concentrations due to extreme point recharge is not affected on calculated recharge (see page 319, Eq. 13c).

Prof. Wood –C4: (a) Mass balance is, however, independent of focused or diffuse flow; mass balance is mass balance!

(b) In this system it might be argued that there are insufficient groundwater sampling points, that the distribution of chloride in the rainfall is not adequately known, or that chloride in rainfall is not at steady state; thus, the CMB is inappropriate. It is not, however, the failure of the CMB approach, only the lack of application of the necessary boundary conditions.

Author Reply: We divide the above comment into two separate responses.

(a) This we agree and acknowledge it on page 315 Line 27.

(b) We appreciate Prof. Wood's comment and concern and agree that multiple groundwater sampling and rainfall measurement stations help to get more accurate groundwater chloride and annual average rainfall (P). Our main concerns are described above in **C1 C2** and **C3** in relation to theoretical aspects and in particular, applicability of the boundary conditions and mass balance, even if the aquifer is fully mixed (let alone heterogeneous).

Prof. Wood –C5: (a) Unfortunately one does not generally know a priori what percentages of recharge are diffuse or focused flow; thus, how many samples to collect. (b) Owing to the unknown, and realistically unknowable, spatial distributions of diffuse and focused recharge areas in most aquifers I fail to see the practicability of the authors deterministic equations, which require basically the same assumptions as the CMB plus additional and difficult to acquire parameters with unknown errors.

Author Reply: We offer the following responses to parts (a) and (b) above.

(a) We agree with Prof. Wood's comment. The main additional parameters that that the generalized CMB requires are point recharge (Q_p), and diffuse recharge chloride (c_{gd}). In our case study basins, clearly defined diffuse recharge zones exit (see details in doi:10.5194/hessd-10-11423-2013 -Hydrological functions of sinkholes..). In the absence of such clearly defined diffuse recharge zones, one has to obtain an estimate of c_u (C_{uz} in Wood, 1999) from chloride extracted from the lower part of the unsaturated zone by coring . In order to get Q_p, one has to estimate surface runoff using an appropriate rainfall-runoff model or by direct measurement in a manner similar to the total recharge estimate of Wood et al (1997).

(b) We acknowledge that the Generalized CMB must include additional parameters to compute the point recharge component and therefore is less staright forward in application when compared to the conventional CMB method. However, our aim is to simplify the physics, while retaining the salient features necessary to describe both the diffuse and point recharge processes.

Prof. Wood –C6: One, however, might be able to develop a stochastic expression based on the standard deviation of chloride concentration with space in an aquifer system that addresses the heterogeneity of recharge and assist in constraining the location and number of samples required to provide a representative regional chloride value.

Author Reply: We look forward to seeing such models developed for groundwater recharge studies.

We thank once again Prof. Wood for participating the discussion forum.

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