Response to comments of Reviewer #6

This reviewer raised a number of issues, including some with our overall approach. Critical comments are always useful as they question assumptions and in the end strengthen the work by having us revisit what we have done. We address the specific questions and concerns below. While these may not answer all this reviewers concerns, we hope it addresses many of them and thank the reviewer for their considered comments.

As to the comments relating to the overall aims of the work. Yes we agree that the hydrograph separations aggregate different components of water and we were clear about that in the introduction with our discussion of what quickflow or baseflow / slow flow might comprise. There are papers that have equated baseflow to groundwater inflows; however, that is not the argument that we set out to address. It was also not our intention to provide a "best" method or (as one of the other reviewers suggested) to train a physical filter to match the chemical data as the two techniques are complementary.

Our aims were to use the mismatches between the two techniques to elucidate processes. Yes, it is true that it has been known for a long time that geochemical techniques commonly yield lower baseflow estimates to techniques such as recursive digital filters. It is also true that the application of any technique is not without uncertainties; however, a number of papers that have assessed this have attempted to make the techniques agree (or have championed one or the other) rather than looking at whether the differences can be useful.

Bank return waters are discussed in the literature but many studies of groundwater-surface water interaction still do not take them into account. There are a number of studies of bank flow (geochemical or otherwise) on a reach-scale or at a specific time. We attempted in this paper to look at the timing and relative importance of bank return water (and other transient sources) over a longer time period and a larger distance scale (so to make it more analogous to the treatment of runoff or baseflow that is based on hydrographs). While the results will always be subject to some uncertainty, there have been few studies to attempt this.

Having read the manuscript and the preceding comments, I am following the scepticism raised by referee # 2. The basic idea of the paper is to compare two different concepts of hydrograph separation: a "physical" one separating quickflow from baseflow and a "chemical" one separating event from pre-event water (using the problematic tracer EC).

As discussed below, EC is not problematic in this catchment.

The underlying concepts of both separations have been known for a long time. None of them separates runoff components by source. Quickflow (direct runoff) and delayed flow (baseflow) have been separated by various methods using runoff data alone (e.g. the well known paper of Hewlett and Hibbert and many others). There is no method that is the "best", all have advantages and disadvantages. The other approach is the well known two component separation into event and pre-event water, because it uses a two-component mixing with two endmembers: the EC-signature of (1) rainfall and (2) low flow. Following the benchmark paper of Sklash et al. 1976, we know that pre-event water can be a major component of direct runoff. This result has stimulated research on runoff generation throughout the world to explain they high fraction of pre-event water in storm

hydrographs. This pre-event water mainly originates from water from saturated zones on the surface or in the subsurface (riparian zones, hillslope groundwater, etc., which is quickly mobilized by piston flow processes. This is true for many catchments. This knowledge is ignored by the paper which becomes clear in the second paragraph of the introduction (ll21-22): "The quickflow component is dominated by event water but can also include older water displaced from soils or the unsaturated zone".

We are not sure that what we wrote in this section is substantially different. Our statement was that older water can form part of the quickflow and the reviewer is correct that the sources mentioned can also contribute to the quickflow. What proportion of quickflow comprises pre-event water probably varies between catchments. In the specific case of the Barwon River, the input of pre-event water causes the rise in the EC as the river discharge rises (as we discuss in the paper). The majority of potential stores of pre-event water, such as the soils and pools on the floodplain have relatively high EC, and it is unlikely that the dilution of EC in the river would occur. In support of this a set of water samples collected during a high flow event in July 2011 have stable isotope ratios that are different to those in the river at other times, implying that this was event water (the data were presented in Cartwright et al., 2013). In other rivers, changes in stable isotope ratios or reduction of radiogenic isotope activities (e.g., Rn or tritium) imply that discharge events have a component of new water. Perhaps it should have been worded more carefully, but what we were trying to say was that the quickflow can comprise a mixture of event water and older water. We have stressed throughout the paper that part of the complication of understanding water balances in catchments is the multiple and possibly changing water sources over a discharge event.

Moreover, it is not true that geochemical data sets are only measured at specific times, e.g. during low flow conditions (p 5947, second paragraph). Again there are many process studies that use the temporal variation of geochemical data and use them as hydrological tracers, e.g. for endmember mixing analysis.

In a similar way to the comment above, we did not mean to imply that geochemical data was only collected at low flow conditions. What we were referring to was the geochemical survey approach where changes to isotope or element abundance along of a series of reaches are used to estimate the spatial variability of baseflow inputs. Such surveys often aim to define the distribution of gaining vs. losing reaches or identify "hot spots" of groundwater infiltration which is easier to do at baseflow conditions. The real point of this paragraph was to highlight a difference between geochemical surveys that generally focus on spatial variability of baseflow at specific times (the paper by Cook 2012 details this) and the techniques that are based on river hydrographs that capture temporal variations but which integrate processes up catchment from the gauge.

Also the obtained hysteresis effects are not new and can partly be explained by kinematic effects: A pressure wave travels along a river and causes the formation of a wave of old water before the new water arrives at the gauging station. How large is this effect in the present study?

Although not expressed in the same terms, this is what we envisaged that the hysteresis loops were showing. The increase in EC during the increase in discharge was proposed to be due to saline water being flushed from the floodplain that was subsequently diluted by the event water. As to the magnitude of this impact, the increase in EC is only observed while the discharge is

increasing and the peak of the discharge event is always characterised by low EC values (hence the old water seems to be flushed from the system before the flood peak).

How much general knowledge do we gain when we compare mathematically separated baseflow with chemically separated pre-event water? For sure the results will be sites specific and will assemble many processes: those that are responsible for pressure driven effects from saturated zones, and others, as stated in the paper, that delay event water, e.g. by bank storage. It is probably impossible to quantify a single process like the present paper attempts.

In the paper, we only quantify bank storage because (unlike other transient sources) it is relatively straightforward to model the timescales over which it operates. Showing that at least one of the transient stores provides water to the river on a suitable timescale to explain the observations was out aim here. We do not make a claim that all the delayed water is from bank storage (although that point could probably be amplified in the conclusions) as we have throughout discussed a number of transient stores. As to the general applicability of this work, we are unaware of many studies that have examined time-series discharge and geochemical data in this way – the results are site specific, but the approach advanced here could be applied elsewhere.

Another point of concern is the use of EC as a chemical tracer. Other reviewers have raised this point already, but it needs to be strengthened once again: EC is NOT a conservative tracer, since it is a physical characteristic of the water and a summary tracer for all dissolved solids. Even when it is claimed that Na and Cl are main components of EC in the study basin, there is no major ion data given to support this statement.

Other reviewers have raised this point, and with hindsight it may probably have been better to use Cl for the chemical mass balance. The correlation between EC and Cl taken from data in Cartwright et al. (2013) shown below has a R^2 of 0.977. We chose to use EC for the mass balalnce as that is what is actually measured; using the calculated Cl values produces closely similar results with little additional uncertainty.
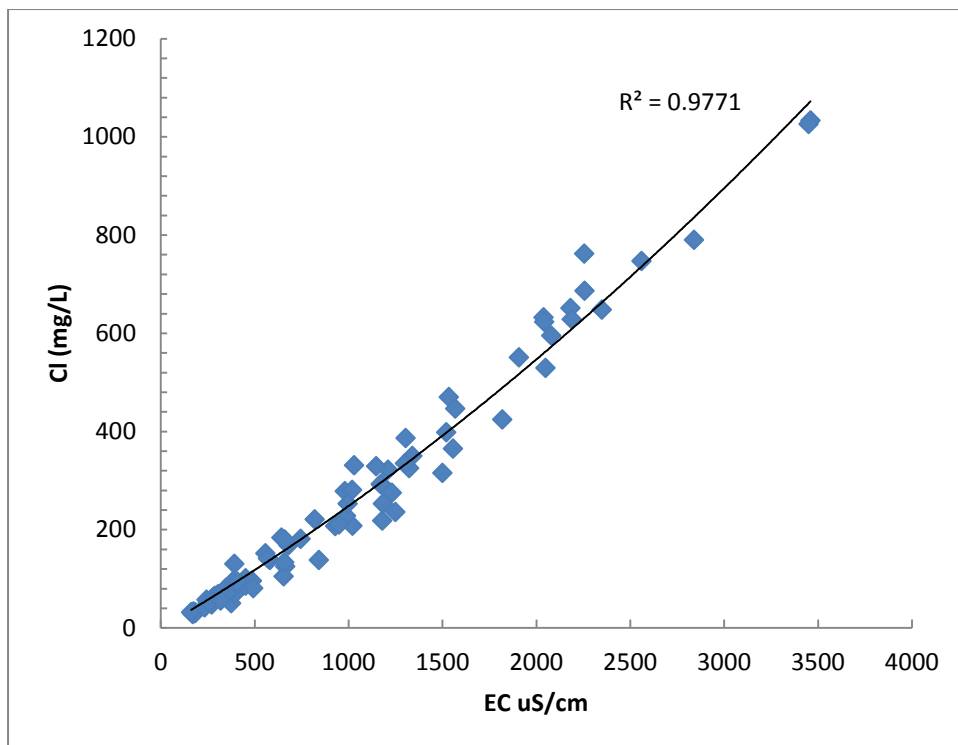
Is the dominance of these two ions really the same also at low EC values?

In all the samples for which we have geochemical data (which represents the range of EC values on the above graph) this does hold true.

It is also admitted in the paper that during times of stagnant water evaporation changes EC values: What is the difference between stagnant flow and the time when the highest EC value was measured? Have the mentioned Isotope samples that are used to exclude evaporation impacts been collected at extreme baseflow conditions? This is especially important, because this value is used as groundwater component for the CMB.

We have stable isotope measurements for a range of flow conditions, even for the baseflow events (represented by the high EC values on the graph above) the maximum displacement of $\delta^{18}O$ values from the meteoric water line is <4‰ with a similar maximum increase in $\delta^{18}O$ values downstream when several samples were measured. This implies <20% evaporation (with much lower values for most samples). These data are discussed in Cartwright et al. (2013), but perhaps more detail is needed in the text.

During times of low flow also biological processes (primary production, etc.) might constantly change EC values.

It is unlikely that biological processes (which typically change NO_3 and DIC) concentrations would produce a sufficiently large change in geochemistry to change EC at the very high EC values under low flow conditions. This assertion is supported by low Nitrate and DIC concentrations (collectively these are <10% of the total anions in the high EC waters).

Last but not least even more important is the limited representativity of the endmembers used for CMB. It is stated that spatially, groundwater EC covers an extremely wide range in the area (1000 –

20000 mikroS/cm). Despite this fact only one (constant) value (3200 mikroS/cm) is used to represent the baseflow "groundwater" component. Strictly speaking, this single value represents one specific mixture of groundwater components over time. This mixture will constantly change during events and during seasons and might change in both directions (not only in one as admitted in the paper). But the entire analysis of the paper is based on the assumption of this constant EC value. This uncertainty is enormous and calls the entire results (especially the seasonal baseflow values) into question.

We address this in a number of our responses. In practice in this and other catchments, it is difficult to be certain of the net EC of groundwater that actually interacts with the river (as opposed to groundwater that is a few tens of metres away) without a density of monitoring bores that is unrealised in many, if any catchments. As with other studies (e.g. Yu et al., 1999; Gonzales et al., 2009) we have used the EC of the river at baseflow to estimate the EC of the groundwater component (Section 4.3). Since the data is for a single gauge, it does represent an estimate of the average EC of groundwater up catchment of that gauge. This is justified on the following grounds.

1. **It is not possible that the net EC is lower than this otherwise the calculated fluxes are negative at baseflow times.**
2. **It is possible to assign a higher EC to the groundwater component but this would have the effect that river at low flows would always have a considerable component of surface water (which is unlikely during the prolonged very low flows).**
3. **In most years the highest EC in the river water during the low flows in the summer is similar. Presuming that this is the time when the river is fed mainly by the regional groundwater inputs, this implies that the EC of the groundwater component at these flow conditions is reasonable well understood.**

In terms of the calculations, assigning the groundwater EC to the maximum EC recorded in the river gives the maximum baseflow flux as calculated by Eq. (3). Nonetheless, this is still considerably lower than the baseflow fluxes calculated by the physical methods. Thus, we have been conservative in our approach and in our comparisons.

Some of this is discussed in Section 4.3, but we can provide additional justification of this point. In particular is important to note that while there is some saline groundwater in the catchment, the average TDS is much less than 13,000 mg/L (EC <20,000 μS/cm); again this can be calcified.

We agree that there is a possibility that the mix of different groundwater components change over time (although there is no a priori reason that is need do so to produce the mismatches that we observed). However, it is difficult to prove either way with data that we have (the area is not particularly data poor and it would be similarly difficult to assess whether a process such as this has occurred in many catchments, not just this one). Many rivers in Victoria have lower salinity groundwater along their floodplains, which largely arises from enhanced recharge from the river during high river stages. It is possible that this reservoir is mobilised following recharge events during wetter periods and we can certainly acknowledge this. This near-river shallow groundwater is analogous to the bank return waters as it originates from the river rather than forming part of the regional groundwater flow system (albeit with probably longer timescales).

Moreover a similar effect is true for the surface endmember which is equated to rainfall EC. Already by the canopy, EC values are increased and this is more extreme when there is contact to the soil surface. This effects have been reported, data exist. So at least a range of values should be used to show the uncertainty of the separation. Probably this uncertainty will mask the influence of bank storage

We do discuss this in the paper. In Section 4.3 we discuss using a higher value of surface water EC in the calculations (100 µS/cm). In terms of what the paper discusses, raising the assumed EC of the surface water lowers the estimates of baseflow from the chemical mass balance technique and thus our assumptions again produce conservative estimates of the mismatch between the chemical and physical techniques. In fact it amplifies not diminishes the need for additional components, such as bank flow. This is noted at the end of section 4.3, but we can reiterate this important point in the Conclusions.